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ABSTRACT BOOK

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S01

INNOVATIVE PROCESSING AND SYNTHESIS

INVITED LECTURES

XVI ECeRS CONFERENCE - Abstract Book

ABS 744

STEREOLITHOGRAPHY: A TRUE MANUFACTURING PROCESS TO BUILD 3D FUNCTIONAL CERAMIC AND CERAMIC/METAL PARTS

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Since their introduction in the late 1980s, additive manufacturing technologies (AM) have become very attractive to produce accurate parts via an automated process. The part is directly built up from a computer-aided-design (CAD) file, allowing the user to have an immediate response on the shape, function or performance of the object. Used in a wide range of industries, AM allows companies to turn innovative ideas into successful end products rapidly and efficiently. Depending on the nature of the final object, the AM techniques can be used to produce a cost-effective single item or a low-volume manufacturing. Today, AM technologies are currently becoming real manufacturing processes in various industrial fields.

In the domain of ceramics, AM technologies constitute an attractive answer to the need of shaping techniques to produce useful complex parts and specific architectures which cannot be produced with a traditional method, without costly tooling and/or machining. Additive processes are likely going to transform the field of ceramic manufacturing and will open new ways of thinking about objects design and fabrication of advanced ceramic with improved or new functions.

Among AM technologies used in the ceramic domain, the space-resolved UV photopolymerization of a reactive ceramic system (Stereolithography) presents the advantage to makes it possible to fabricate useful, dense complex 3D objects, with a high dimensional resolution, a good surface finish and properties similar to those obtained by classical routes. This process is used to design and fabricate innovative advanced ceramic components for various applications (space, telecommunication, biomedical, engineering, jewellery…) requiring specific properties.

The understanding of the main parameters that influence the polymerization (kinetics and conversion rate) and the lateral and depth resolution of the reactive system, associated with the prediction of the final dimensions and stiffness of the green part obtained by numerical simulation, now allows to directly elaborate ceramic components with high dimensional accuracy and good surface finish.

Hybridization of additive manufacturing processes could find a major interest in the manufacture of 3D multi-material parts. In this respect, stereolithography, associated to micro-extrusion, offers the opportunity to manufacture 3D ceramic/metal parts in order to answer identified industrial needs, particularly in electronic domain (HTCC and LTCC). It becomes yet possible to build components with intricate metal conductive networks that cannot be obtained by classical tape casting and screen-printing route.

Keywords: Stereolithography,Polymerization,Hybridization

ABS 722

DESIGN OF NANOSTRUCTURED RE-DOPED CERAMICS WITH IMPROVED OPTICAL PROPERTIES PREPARED BY DIFFERENT SYNTHESIS ROUTES

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Lanthanide cations such as Eu3+ and Tb3+ offer outstanding optical, magnetic, and bio-affinity properties, and not surprisingly are being widely used for example as up conversion materials, catalysts, and fluorescence labels for biological detection. If they are fabricated in the form of nanorods, nanowires or hollow spheres, their luminescent efficiency and display resolution are further enhanced as a result of both their marked shape-specific and quantum-confinement effects. Among various possible hosts for lanthanide dopants, LaPO4 is noteworthy due to the potential high light yields of the resulting doped materials. In order to design the above-mentioned morphologies specific chemical synthesis methods have been developed and are considered in this study.

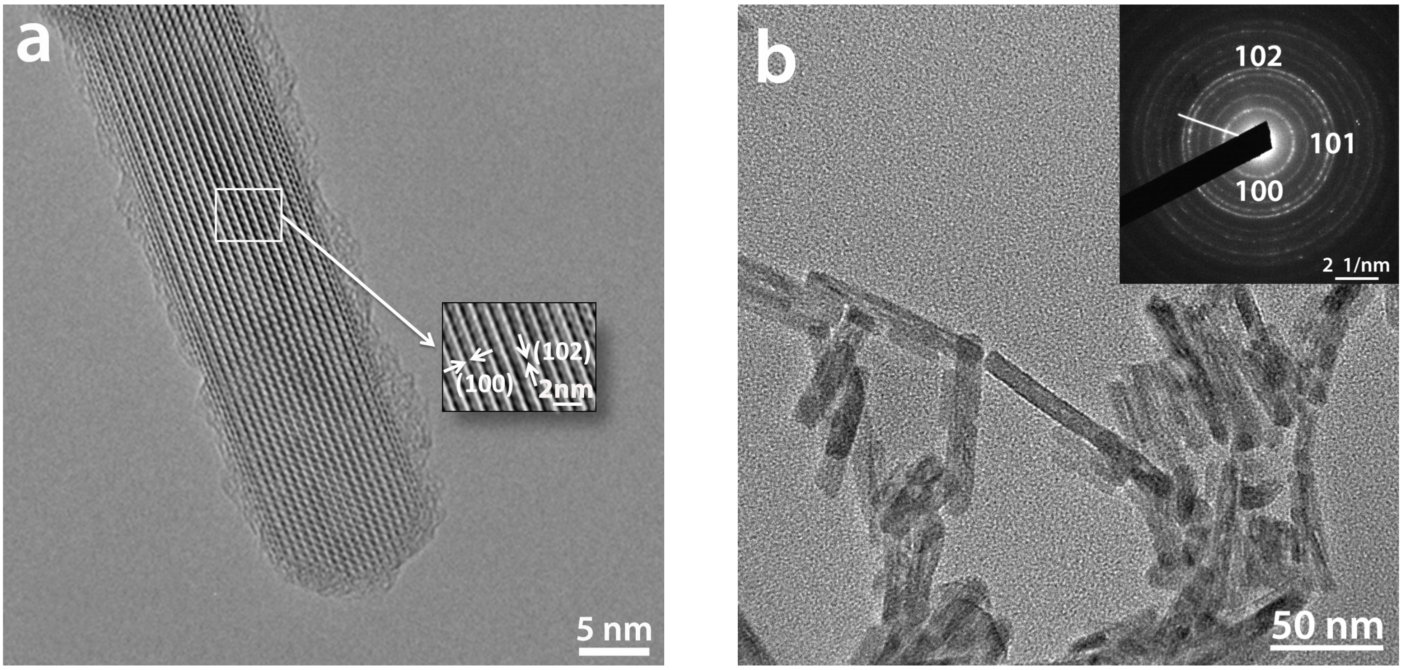

Fig.1. a) HREM micrograph of as-prepared rhabdophane and TEM micrograph of Tb3+-doped rhabdophane nanorods prepared by microwave-assisted hydrothermal synthesis.

Keywords: microwaves, hydrothermal synthesis, sol-gel

ABS 654

SOL-GEL PROCESSING OF NOBLE METAL OXIDES NANOSTRUCTURED COATINGS FOR ENERGY RELATED APPLICATIONS

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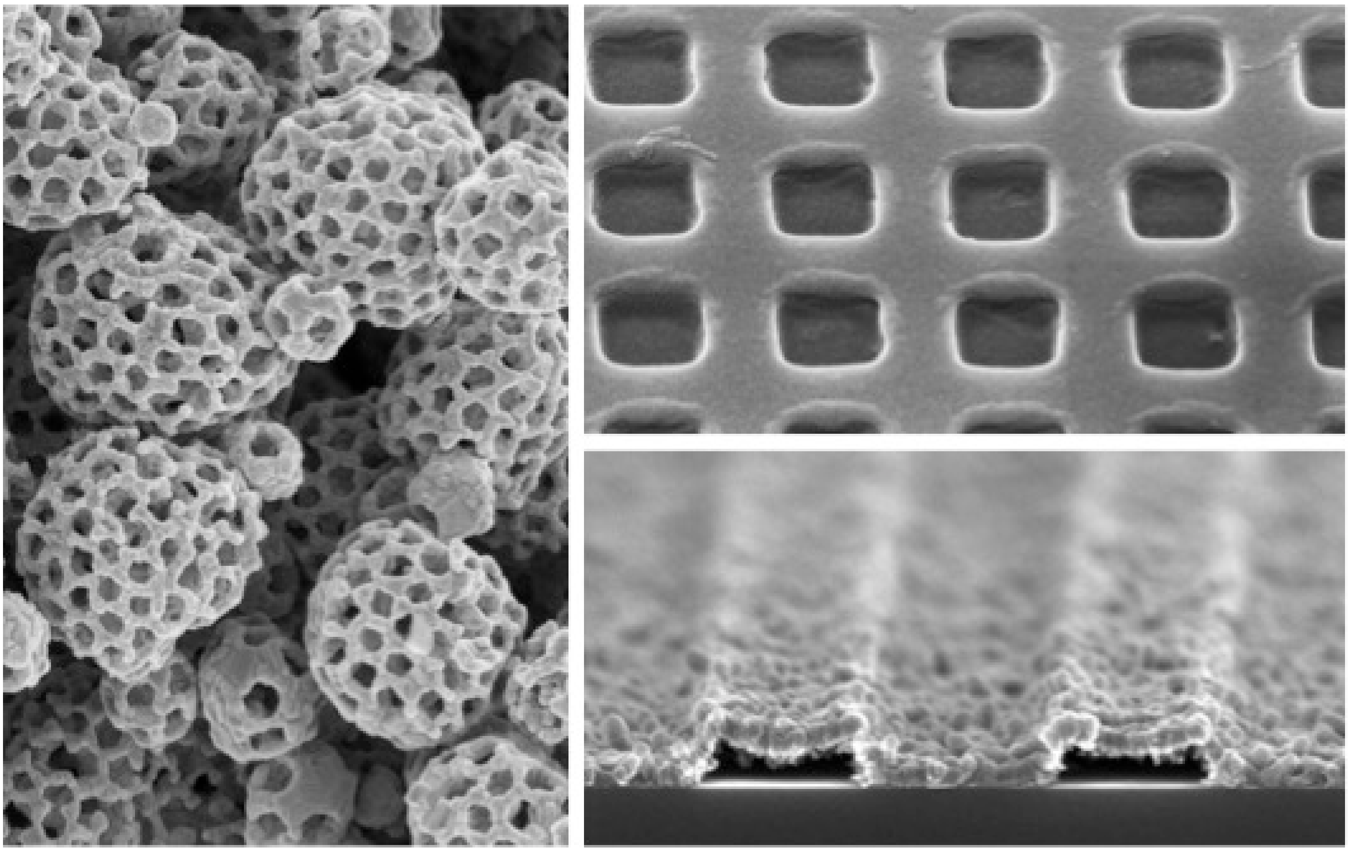
Noble metal and metal oxides (Ir, Pt, Ru, Rh...) are of major interest in all the energy-relevant domains such as catalysis, electrocatalysis, photocatalysis, fuel cells and batteries, and separation processes. However these materials are generally obtained as discrete spherical particles and reshaping them by conventional methods is challenging. However, adding a further structuration such as porosity would be highly beneficial (i) to decrease the metal loading, (ii) to increase the surface area and (iii) to optimize the diffusion and confinement regimes.

In this talk, I'll discuss the "underexplored" sol-gel chemistry of "noble metals" that can be coupled with solution-processing. The key idea is to develop inorganic nanomaterials with complex compositions, behaving as metals, thermally and chemically resistant and shaped at the nanoscale as polymers through evaporation induced self-assembly and/or lithographic methods.

The versatility of the methodology will be described by 2 examples. In the first example, sol-gel based Ir/IrOX and Metallic Iridates spheres with hierarchical porosity were obtained by spray-drying and used as building block to fabricate outstanding catalytic layers for electrolysis. In the second examples, noble metal oxides films were patterned by a range of lithographic methods and used as highly resistant nano fabrication masks, nanofluidic channels and electronic contacts.

These chemical strategies were developed thanks to in-situ analytical methods such as in-situ-TEM and synchrotron X-ray absorption and scattering techniques.

Keywords: Sol-gel, Templating, Noble Metals



ABS 635

RELATIONSHIP BETWEEN PROCESS, MICROSTRUCTURES AND PROPERTIES OF HIGHLY POROUS CERAMIC INSULATORS PREPARED BY GELATION FREEZING ROUTE

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Macroporous ceramics having unique pore morphologies with ceramic bridges, honeycomb and bamboo-like cells were fabricated by freezing gels with ceramic powder and various gelatin contents. Varying gel strengths were found to be effective for control of the pore architecture from open to closed pore channels. The proposed process is a relatively simple and versatile way to produce tailored pore configurations via a gelation freezing route. In addition, the relationship between the microstructures, thermal conductivities and mechanical properties of the resulting ceramics was discussed using a multiscale modeling technique, in which a homogenization method was conducted with microscopic models created from 3D images, temperature or stress distributions in macroscopic samples by FEM and their local distributions. The simulation results were consistent relatively with the experimental results. The multiscale modeling technique was thus confirmed to be a strong tool for prediction of the mechanical responses of porous ceramics.

Keywords: porous ceramic, thermal insulator, modeling

ABS 528

POLYMER-DERIVED COBALT-DOPED AMORPHOUS SILICA NANOCOMPOSITES WITH HYDROGEN AFFINITY

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Microporous amorphous silica membranes are well known for their excellent high-temperature hydrogen permselectivity at 500 °C. Recently, transition metal cation-doped amorphous silica membranes have been found to show a selective enhancement in the hydrogen permeance at middle temperatures ranging from 300 to 500 °C. Moreover, compared with Ni, Co-doping was effective for enhancing the hydrogen permeance. The mechanism for the enhancement was thought to be explained by the intrinsic hydrogen affinity of transition metal nanoparticles formed in-situ within the silica matrix during the membrane synthesis from the metal-organic precursors up to 600 °C in air followed by the high-temperature H2 permeation test at 500 °C. However, the Co species within the silica matrix after the hydrogen permeation test were found as both metal Co and CoO-like oxides, and the resulting hydrogen capture capacity at 500 °C of the Co-doped amorphous silica was much lower than that of Ni metal nanoparticle-dispersed silica. In this study, to clarify the dominant mechanism, Co cation-doped amorphous silica materials were designed and synthesized through the Polymer-Derived Ceramics (PDCs) route, and characterized in terms of the oxidation state of Co species within the amorphous silica matrix, and chemical affinity toward hydrogen. At the Co/Si atomic ratios of 1/80, 1/40, 1/20 and 1/8, commercially available perhydropolysilazane (PHPS) in xylene solution was modified with Co(acac)3 at 110 °C to afford a single source precursor for the multicomponent Si-Co-C-O-N system. The ATR-IR spectroscopic analysis suggested possible chemical bond formation via the hydrometalation between Co(acac)3 and PHPS . The single source precursor was exposed to air in the presence of ammonia vapor at room temperature, and subsequently pyrolyzed in air at 600 °C to afford X-ray amorphous Co-doped silica at all the Co/Si atomic ratios ranging from 1/80 to 1/8. The nanostructure of these samples were carefully observed by TEM and STEM, and Co species were observed as amorphous particles finely dispersed within the silica matrix. The particle sizes within the samples having Co/Si atomic ratios up to 1/8 were approximately 2 to 3 nm. Both TEM-EELS and XPS analyses revealed the dominant oxidation state of Co in the samples as divalent. On the other hand, DRIFTS analysis detected an apparent absorption band broadening at around 3750 cm-1, which was due to the hydrogen bond formation of Si-OH groups. These results suggested that, in addition to amorphous nanoparticles, the doped Co existed as Co (II) cation which modified silica matrix at the Si-OH groups. At the presentation, the hydrogen affinity of the Co (II)-SiO2 evaluated by measuring the deuterium self-diffusion coefficient will be shown and discussed aiming to clarify the dominant mechanism for the selective enhancement in the hydrogen permeance observed for the Co-doped amorphous silica membranes.

Keywords: Co-SiO2, Hydrogen affnity, Polymer-Derived Ceramics

ABS 362

MANUFACTURE OF SUPERCAPACITORS OF METAL TRANSITION OXIDES AND GRAPHENE BY ELECTROPHORETIC DEPOSITION

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Supercapacitors are devices that store energy and supply energy at a high rate. Compared with batteries and fuel cells, supercapacitors are able to reach high specific power but low specific energy, and high cycling and low equivalent series resistance. Ppseudocapacitors are one of the different types of supercapacitors charaterized because they store charge by redox reactions. Typically used materials are transition metal oxides, such as MnO2, RuO2, IrO2, etc. Among them, MnO2 is much cheaper although it has lower capacitance values and lower conductivity. The other are too expensive to be used in industry. Other posible transition metal oxides need to be checked as possible candidates for this application. One of them is SnO2. Graphene nanoplatelets have been used as secondary phase for enhancing the electrical conductivity which is low for those oxides.

This work deals with the preparation of electrodes for supercapacitors consisting of either manganese oxide or tin oxide supported onto graphite by aqueous electrophoretic deposition. The starting oxide powders were characterized and dispersed in water by controlling the colloidal and rheological behavior in order to obtain stable suspensions. Optimized manganese oxide or tin oxide suspensions were deposited onto graphite electrodes by EPD. The deposited mass per unit area in the electrodes was optimized by controlling the applied current density and the deposition time. It has been demonstrated that the introduction of a binder helped to improve the adherence to graphite; otherwise the deposit thickness obtained by EPD is limited and no films can be obtained by simply dipping. In a second step suspensions of each metal oxide with graphene nanoplatelets were prepared and optimized for the electrophoretic codeposition. The obtained coatings were characterized in terms of capacitance and specific energy. The results for SnO2 and MnO2 were compared as well as the effect of graphene addition on the electrochemical properties.

Keywords: Electrophoretic deposition, Metal transition oxides, Supercapacitors

ABS 218

ADDITIVE MANUFACTURING AND STRUCTURAL CONTROL OF CERAMICS

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Additive manufacturing technologies have created new opportunities for the fabrication of ceramic parts with designs that cannot be realized using standard processing technologies. Therefore, it is not surprising that it has attracted much interest in the ceramic field. However, to ensure optimum performance it is necessary to control not only the macroscopic shape but also the structure at multiple length scales from the nano to the macro levels. This presentation will review the opportunities and challenges opened by additive manufacturing in the structural control of ceramic-based materials including microporous ceramics, fibre reinforced materials or ceramic composites with bio-inspired architectures. One particular challenge is the fabrication of multimaterial structures. The goal is to trigger a discussion and identify concepts that will guide the development of ceramics additive manufacturing.

Keywords: Additive Manufacturing, Microstructure

ABS 198

STATE OF THE ART IN LITHOGRAPHIC ADDITIVE MANUFACTURING OF CERAMICS

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This contribution focuses on new developments in the field of the lithography-based ceramic manufacturing (LCM) process. Among the different additive manufacturing (AM) techniques for ceramic materials, lithographic technologies are widely used in industrial applications for the processing of high-performance ceramics due to their high precision and the good material properties that can be achieved because of the high green density and the two-stage nature of the process (separated shaping and sintering).

These industrial applications range from human bone implants for regenerative surgery, over ceramic casting cores for the fabrication of turbine blades, to high-performance ceramic components for different kind of technical applications such as nozzles, mixers, and guides.

Furthermore, a broad range of different materials can already be processed by the LCM technology. While darker powders are more difficult to process due to the light absorption and scattering phenomena. But by optimizing the photocurable suspensions towards very high reactivity the printing of materials such as silicon nitride could already be realized. It is shown that 3D printed silicon nitride-based ceramics achieve the same mechanical properties as conventionally formed components. In the area of oxide ceramic materials, it could already be demonstrated that lithographic AM can be used to fabricate translucent alumina parts with a fully dense microstructure and grain size below 500 nm, underlining the extremely high quality of printed parts that can be obtained by using lithographic AM techniques. In combination with the high resolution and good repeatability of lithographic AM this technology opens up new possibilities in terms of feasible geometries and designs and first examples of such designs that are already being used in industrial environments are presented.

Keywords: stereolithography, industrial applications

ABS 940

HIERARCHICAL POROUS CERAMICS MADE BY 3D PRINTING

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Hierarchical porous ceramics are attractive structures for a variety of applications due to their high surface area combined with enhanced permeability. However, synthetic porous ceramics have not yet reached the elaborate architectural design and high mechanical efficiency found in natural porous materials like bamboo, bone and wood. To fill this gap, processing routes that enable deliberate control over the material's porous structure at multiple length scales are highly demanded. In this talk, I will show how 3D printing technologies can be explored to fabricate hierarchical porous ceramics with unprecedented mechanical efficiency and architectural control. The key feature of our approach is to design emulsion or foam-based inks whose droplet/bubble sizes are sufficiently stable to withstand the shear forces developed in the printing process, while later serving as a template for the macropores generated after drying and sintering of the printed object. This methodology enables independent tuning of porosity and pore sizes at multiple length scales, resulting in enhanced mechanical efficiency. To demonstrate the potential of the process, we 3D printed emulsion/foam inks into parts with complex geometries and bioinspired multiporosity features that cannot be achieved through conventional processing.

Keywords: 3D printing, porous ceramics, hierarchical materials

ABS 89

TEXTURING OF YTTRIA AND CERIA STABILIZED TETRAGONAL ZIRCONIA POLYCRYSTALS IN A 17 TESLA MAGNETIC FIELD

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In prior work we have shown that tetragonal zirconia powder cannot be aligned by applying a strong magnetic field during green forming of a powder compact. However, a strong texture can be achieved in 3 mol percent yttria stabilized tetragonal zirconia polycrystals (3Y-TZP) by using a reactive texturing technique. One uses a suspension that contains monoclinic zirconia which can be oriented in a strong field during green forming for instance by slip casting. The monoclinic (100) plane is oriented perpendicular to the magnetic field direction. When a mixture of pure monoclinic zirconia powder and 8 mol% yttria co-precipitated zirconia is used, a strong texture of single phase 3Y-TZP is obtained after reactive sintering for 3 hrs at 1650°C. The (001) plane of the tetragonal phase is perpendicular to the magnetic field direction, i.e., the c-axis is aligned parallel to the field. In the strong magnetic field of 17.4 T used in the present work, the texture of the cast green ceramic, can be measured (Lotgering factor $f = 0.15$) whereas at lower fields texture in the green body is barely discernible. After sintering a Lotgering factor of 0.8 is measured. More detailed analysis of the texture showed a texture index of 32.5.

We attempted to texture ceria stabilized tetragonal zirconia polycrystals (Ce-TZP) by a similar strategy but with less success. The suspension consisted of a mixture of monoclinic zirconia and nanometric ceria powder. Orienting the monoclinic zirconia particles during slip casting was again clearly achieved with a Lotgering factor of 0.3 calculated from the monoclinic reflections again with the (100) plane normal to the magnetic field. After reactive sintering a single phase tetragonal microstructure is formed if the sintering temperature is chosen high enough. However the resulting Lotgering factor for the 001 reflections was only 0.3 and a texture index of about 3 was measured.

It appears that for successful reactive texturing of zirconia the differences in composition between the monoclinic phase and the phase containing the stabilizing element should be as small as possible.

Keywords: Texturing, reactive sintering, zirconia

ABS 50

TUNING MICROPOROUS CERAMIC MEMBRANES FOR SOLVENT NANOFILTRATION

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Membranes, based on ceramic materials, are interesting because of their robustness and can therefore be applied under several demanding conditions, like recovery of products or (organic) solvents. Not only robustness is important but also pore size as well as membrane-solvent-solute interactions are important to obtain membranes with the required separation properties. In our work alumina membranes are designed for the nanofiltration of organic solvent solutions with a focus on non-polar solvents. In order to achieve both the desired pore size and surface properties, two different polymer grafting methods will be discussed.

Firstly, we developed a new type of nanofiltration membrane by grafting small PDMS polymer chains into the 5 nm diameter pores of a γ-alumina ceramic layer, which rests on an α-alumina support (pore size 80 nm). By applying this so-called “Grafting-to” method of PDMS in the ceramic pore, these membranes exhibit particular transport phenomena due to the localized (in-pore) swelling of the PDMS. The degree of swelling is solvent-dependent, which impacts both the solvent permeability and the solute retention of the membrane [1].

Secondly, polymerization of styrene from a surface-bound initiator is demonstrated (= Grafting-from). Surface-Initiated Atom-Transfer Radical Polymerization (SI-ATRP) is used to grow polystyrene brushes of low molecular weight (1kDa - 5KDa) inside the 5 nm diameter pores of the γ-alumina layer. We demonstrate tailored shrinking of these pores by varying the reaction conditions of SI-ATRP, such as solvent or reaction time. The results of these Grafting-from reactions were characterized with FTIR, nitrogen adsorption/desorption and TGA. The membranes exhibit high separation performance with a toluene permeability of 3.5 L m-2 h-1 bar-1 and 70% rejection of a 330 Da solute [2].

In conclusion, the inherent chemical and mechanical resistance of ceramics coupled with the multitude of possible grafts can result into three major benefits for grafted ceramic membranes: long membrane lifetimes, suitability to harsh conditions, and the ability to be tailored to a large range of applications.

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Keywords: Ceramic Membranes,Nanofiltration,Polymer Grafting

ABS 6

ADDITIVE MANUFACTURING OF SILICON CARBIDE BY LSD-PRINT

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The layerwise slurry deposition (LSD) has been established in the recent years as a method for the deposition of ceramic powder layers. The LSD consists in the layer-by-layer deposition of a ceramic slurry by means of a doctor blade; each layer is sequentially deposited and dried to achieve a highly packed powder layer. The combination of binder jetting and LSD was introduced as a novel technology named LSD-print. The LSD-print takes advantage of the speed of binder jetting to print large areas, parallel to the flexibility of the LSD, which allows the deposition of highly packed powder layers with a variety of ceramic materials.

The working principle and history of the LSD technology will be shortly discussed. A theoretical background will be also discussed, highlighting advantages and drawbacks of the LSD compared to the deposition of a dry powder.

The last part of the talk will be dedicated to highlight recent results on the LSD-print of SiSiC of geometrically complex components, in collaboration between BAM and HC Starck Ceramics GmbH. Density, microstructure and mechanical properties of LSD-printed and isostatic pressed samples will be discussed and compared.

Keywords: Layerwise slurry deposition,Silicon Carbide,Additive Manufacturing

S01

INNOVATIVE PROCESSING AND SYNTHESIS

ORAL PRESENTATIONS

ABS 860

MAGNETITE MESOCRYSTALS SYNTHESIZED THROUGH REDUCTIVE HYDROLYSIS AND THEIR MAGNETORHEOLOGY

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We report a facile synthetic method for spherical magnetite mesocrystals and their possible applications. The spherical magnetite mesocrystals can be obtained by reductive aging of an iron oxyhydroxide in in ethylene glycol. It is noted that any organic additives such as surfactants and polymers are not employed. To the best of our knowledge, this is the simplest way for magnetite mesocrystals. The structural examinations revealed that the spheres were a dense assembly of the primary particles of which dimeter was of several tens of nanometers. The selected-area electron diffraction pattern of this individual sphere displayed a single crystalline-like structure of magnetite. This pattern indicated that the whole microsphere was three-dimensional assembled by primary particles along the same crystallographic orientation, which was in agreement with the characteristics of mesocrystals. The magnetic saturation values measured at 300K was about 80emu/g. The time-resolved evolution of the iron oxyhydroxide to the spherical magnetite mesocrystal was tracked, and its transformation pathway was deduced. Moreover, to examine the feasibility of the spherical magnetite mesocrystals for a field-responsive material toward soft-robotics, magnetorheology was investigated for their dispersed colloid.

Keywords: Mesocrystal, Magnetite, Reductive hydrolysis

ABS 837

POROUS SHAPE MEMORY ZIRCONIA BY GRADIENT-CONTROLLED FREEZE CASTING

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Partially stabilized zirconia exhibits shape memory and superelastic properties which are useful in engineering applications such as sensing, actuation and energy damping. However, due to the strain mismatch during the martensitic phase transformation, polycrystalline zirconia-based ceramics fail after only several deformation cycles. Recently, small volume (< 0.5 μm^3) single crystalline or oligocrystalline structures showed enhanced shape memory and superelastic properties[1], and cyclic superelasticity with more than 100 cycles has been reported[2]. This concept can be adapted to create macroscale shape memory ceramics by creating porous structures which provide higher surface area-to-volume ratio than bulk form, and hence, enable stress relief during the transformation.

In this work, directionally aligned porous structures are created via freeze casting of ceria-doped zirconia. In particular, unlike in the previous study on freeze casting of shape memory zircoania[3], the temperature gradient is controlled, in addition to freezing velocity, such that a honeycomb porous morphology can be created with high mechanical strength to facilitate shape memory properties without premature fracture. The pore morphology change by freezing condition is investigated by scanning electron microscopy, and the shape memory properties is evaluated by compression test followed by x-ray diffraction analysis.

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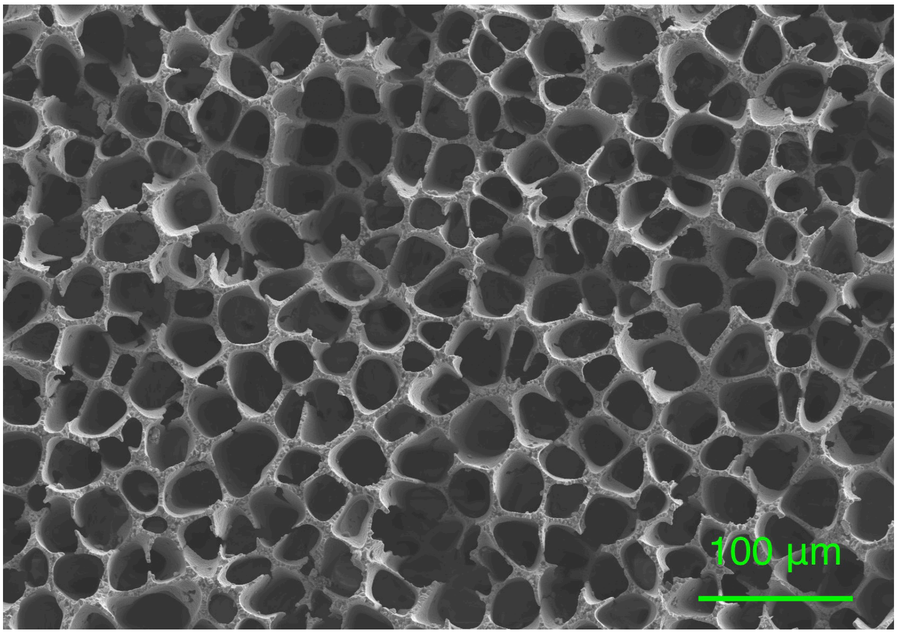
Keywords: Ice-templating, Shape memory effect, Martensitic transformation



ABS 836

REALISATION OF SILICON CARBIDE PIECES BY ADDITIVE MANUFACTURING

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Silicon carbide is a non-oxide ceramic who has great mechanical properties, chemical inertia and a thermal tolerance making it a perfect candidate for many applications (spatial, aeronautics, medical, filtration membranes, …). The main limit of Silicon carbide is the sintering process followed by an expensive cost of machining to get the required dimensions for the pieces. For reducing time and price of production and also obtaining more complex geometry it's necessary to develop new manufacturing methods.

Robocasting technology and Binder-Jetting technology have been selected to respond to this.

Robocasting uses a plastic or metal wear to be unwind from a coil through a moving, heated printer extruder head and supply material to produce a layer. At C.T.T.C. an Robocasting machine has been customized to use ceramic paste instead of heat-meltable wear as ceramic cannot be fused in those conditions. So, rheological properties were studied in order to get an extrudable ceramic feedstock through the printing nozzle. To do so, formulation and manufacturing parameters have been adjusted to make a feedstock based on a silicon carbide powder for Robocasting application.

Binder-jetting is a technique that consists of ejecting a solvent containing an organic binder which will be deposited layer by layer on a powder bed, in order to produce a 3D object. Additive manufacturing by binder-jetting requires a well-controlled powder formulation. No support is needed, this function being assumed by the powder bed itself which allows to create complex and airy structure. Thus, we managed to create some great fineness pieces with small size and complex design composed of silicon carbide.

Following the shaping step by Robocasting or Binder Jetting 's the debinding and sintering stages have to be perfectly controlled for obtaining ceramic components of quality.

This talk, focused on the additive manufacturing of Silicon Carbide pieces for various application will show the potential of these two different technologies.

Keywords: Silicon Carbide, Robocasting, Binder-jetting

ABS 833

SELECTIVE LASER MELTING OF CERAMIC COMPOSITES

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The key engineering ceramics (metal borides, carbides and nitrides) can be utilized for additive manufacturing with the help of a proper design of internal structure, in particular, for selective laser melting. The advanced hard and refractory ceramic composites, such as TiB2/Si3N4, TiB2/TiN, BN/TiC, MoSi2/Si3N4, etc., are in the focus of considerable attention for a number of functional and structural applications including heat sinks, bio-scaffolds for tissue engineering, cutting tools, wear-protective coatings. However, finishing advanced hard materials into intricate shapes with the required tolerance is often extremely difficult, expensive and time-consuming task. Drawbacks of low laser absorption and irregular structure and size of ceramic particulates can be overcome if core-shell structured composite powders of a controlled particle distribution are used. In ceramic-metal(metalloid) core-shell particles, the ceramic core provides mechanical properties, and metal/metalloid shell promotes the laser absorption and improves the densification process. For the production of core-shell powders for AM process, an energy saving and advanced synthesis method, self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS), was utilized. In the present study, combustion synthesis of TiB2, MoSi2 and BN based refractory composites was implemented. Combustion synthesis was performed based on thermodynamic consideration in the selectively chosen reactive mixtures to ensure a sufficient quantity of liquid metal/metalloid phase to cover ceramic particulates and at a moderate temperature to provide the evolution of fine particles. The effect of initial mixture composition, sample geometry and external gas pressure on the combustion features, products phases and microstructural features were examined. Bulk and complex geometry TiB2, MoSi2, BN based materials with high (up to 90wt.%) content of ceramic phase particular emphasis on microstructure were developed. The result was disclosing the crucial role of metal-metalloid amount on the combustion laws, and the effect of laser current on the sintering behaviour and mechanical properties of bulk samples. The relative density of about 97% of solid parts was achieve. The volumetric energy density of SLM laser has remarkable influence also on the lattice structure's strength, volume fraction and density. Under compressive test, samples sintered using a higher laser current exhibit a higher strength value.

Keywords: combustion synthesis, selective laser melting, ceramic composites

ABS 829

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF TiC_4-B_4C COMPOSITES PREPARED BY ADDITIVE MANUFACTURING

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Heavy duty transportation into space requires reduction in mass while enhancing fuel efficiency to achieve higher payloads. Such a performance can be achieved by taking advantage of the properties offered not only by new spacecraft and propulsion technologies, but also by application of nano- or multi-materials and by developing new manufacturing methods. The Machine for Multi-Material-Manufacturing ("4M-System") developed by RHP-Technology GmbH was used for preparation of boron carbide (up to 10 vol. %) reinforced Ti-6Al-4V alloy. The ability to transfer commercial plasma transfer arc (PTA) process into the family of additive manufacturing technologies enables to produce large and complex multi-material 3D components. In this work the composite structures of Ti64-B4C were deposited onto substrate from powder feedstock using RHP's 4M System under protective argon atmosphere. An in-situ reaction between melted titanium based alloy and B4C particles resulted into matrix reinforcement preferentially in a form of TiB whiskers. The results show an improvement of Young´s modulus in parallel (x-direction) as well as perpendicular (z-direction) to build-up direction from 110 GPa for Ti64 alloy up to 164 GPa for Ti64 with 10 vol. % of B4C particles added. The ultimate tensile strength on the other hand dropped to 574 MPa and 554 MPa in both orientations with zero elongation at break what indicates ceramic like fracture behaviour. Aside from mechanical properties the influence of B4C amount on the microstructure of manufactured parts was investigated.

Keywords: Additive Manufacturing, Boron Carbide, Titanium Composites

ABS 828

DEVELOPMENT OF A CERAMIC-CERAMIC WELD BY PLASMA SPRAY

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Aluminosilicate powders are used in plasma spraying mainly as coatings of no more than a few millimeters thick. These coatings have high dielectric strength, high hardness, good wear resistance, excellent refractory properties, they are chemically stable. However in the case of ceramic-ceramic welding, aluminosilicate powders are very hard to spray in coatings of tens of millimeters due to the high thermal shock that can induce damage at the microscopic and macroscopic scales in both weld and ceramic support. The aim of this study, supported by Andra under the “Investments for the Future Program”, is to weld dense ceramic parts through means of plasma spray, by controlling the heating, spraying and cooling procedures. Moreover, several compositions with different ratio of alumina to silica are tested in order to reduce thermal expansion coefficients mismatch. The heating and cooling procedures are optimized using a numerical model in order to limit the thermal stresses generated within the ceramic support. Mechanical tests are performed on the weld as well as on the ceramic support in order to determine their compatibility.

Keywords: Ceramic welding, Thermomechanical analysis, Numerical modeling

ABS 819

FABRICATION AND PROCESSING OF THE LANTHANUM DOPED PZT THIN FILMS ON Pt(111)/Ti/SiO_2/Si(100) AND GALLIUM-DOPED ZINC OXIDE COATED GLASS SUBSTRATES

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In this study, the precursor solutions of Pb(ZrxTi1-x)O3 (PZT) and (Pb1-xLax)(Zr1-yTiy)1-x/4O3 (PLZT) were prepared. Then, thin films were deposited by spin coating method on Pt(111)/Ti/SiO2/Si(100) and gallium-doped zinc oxide (GZO) coated glass substrates. Effect of the x=8%, 9% and 10%-mole lanthanum addition to A site in PZT structure, the effect of the interlayer pyrolysis steps and annealing temperature on crystallization, microstructure, optical and ferroelectric properties have been investigated as the main parameters. %2-mole and %5-mole excess Pb was added to PZT and PLZT solutions, respectively. The films were annealed at 600°C to 725°C for 1 hour called as rapid thermal annealing (RTA). For the Pt(111)/Ti/SiO2/Si(100) substrate. It was obtained by X-ray diffraction that, annealing of the PZT thin films at 700°C for 1 hour resulted with perovskite structure and no secondary phases. This annealing temperature was increased to 725°C for the films coated on GZO coated glass substrate. The thickness of the 5-layered films were measured as ~530 nm with scanning electron microscope (SEM). From the optical band gap calculations, PZT and PLZT thin films coated on GZO coated glass substrates had ~4.2 eV band gap value. Transparency levels were measured as %50 and %60 for the PZT and PLZT thin films respectively, for their best-crystallized processing conditions. The leakage current level of the PZT films obtained on Pt(111)/Ti/SiO2/Si(100) substrates was found to be as 5x10-10 A/cm^2 at 20 kV/cm. Also, Curie temperature (Tc) of the PZT thin film fabricated at 700°C for 1 hour was measured as 330°C.

Keywords: sol-gel, PZT, PLZT

ABS 815

MULTIFUNCTIONAL 3D PRINTED CELLULAR Cr_2AlC MAX-PHASE ARCHITECTURES

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Objective Cr2AlC MAX-phase is an attractive material for high-temperature applications due to its excellent oxidation and corrosion resistances, self-healing ability and high thermal conductivity. The development of three dimensional (3D) cellular MAX-phase architectures would allow widening their use for high performance applications in the energy, transportation and aerospace fields. Therefore, the aim of this work is double: first, to manufacture 3D Cr2AlC MAX-phase scaffolds by means of Robocasting, a direct ink writing technique, and, secondly, to analyse their electrical, mechanical, and thermal properties as well as their oxidation resistance.

Materials & Methods The 3D printing of Cr2AlC scaffolds first requires the development of a printable ink. In this way, a highly concentrated aqueous ink was formulated by mixing Cr2AlC powders with different organics agents. A deep rheological study was performed to set the water, solid and organics concentration. Cuboid Cr2AlC periodic lattices were computer designed and reproduced with a custom three-axis robocasting system. The as-printed scaffolds were heat treated to burn-out the organics and, afterwards, pressureless spark plasma sintered to densify the MAX-phase skeletons.
A complete microstructural characterization was carried out using X-ray diffraction and scanning electron microscopy techniques. The mechanical and electrical properties of the Cr2AlC scaffolds were determined by compression tests and the four probe dc method, respectively. Besides, the 3D structures were heated using a micro-torch gas burner and the temperature cooling profile was recorded as a function of time using a thermal imaging infrared camera. Finally, scaffolds were heated at 1100 °C for 2h and cooled at room temperature for 15 min during 200 cycles to check their thermal oxidation resistance.

Results The formulated ink presented a shear thinning behavior with high storage modulus (~105 Pa) and yield stress (>100 Pa) that enabled retaining the filamentary shape and avoided the collapse of the built 3D structures. The 3D printed cuboid Cr2AlC periodic lattices exhibited high porosity (~70%) and low density (~2.0 g·cm-3), as well as high compressive strength (65 MPa) and electrical conductivity (> 105 S·m-1). The structures survived the thermal cycling tests with no signs of degradation, and also showed low thermal inertia with cooling rates above 1300 °C·min-1.

Conclusions 3D Cr2AlC MAX-phase architectures were successfully printed using a direct ink writing technique. The 3D scaffolds exhibited multifunctional properties, including good mechanical and thermal oxidation resistances, and high thermal and electrical conductivities.

Keywords: 3D printing, MAX-phase, Multifunctional properties

ABS 809

COMPOSITE $Al_2O_3/SiO_2/CaO$ FOAMS REINFORCED WITH CELLULOSE ACETATE FIBRES FROM CIGARETTE TOWS

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Discarded cigarette tows (CTs) are a form of non-biodegradable litter, representing a serious environmental concern. In this work, a reactive foaming technique for the fabrication of stiff and low-cost ceramic foams, reinforced with cellulose acetate fibres recycled from derived from CTs, is illustrated.These were mixed with aluminium powder, calcium hydroxide and aqueous sodium silicate, forming a viscous suspension, which upon foaming, set into a stiff green . The resulting foams exhibited densities ranging from 0.2 to 0.4 g/cm^3. XRD analysis showed how the inorganic matrix was prevalently composed by unreacted Al (~ 17 wt. %), Ca(OH)2, Al(OH)3 and a significant amount of amorphous phase (~ 48 wt. %). The tomographic reconstruction revealed that samples were characterized by a wide pore size distribution These materials exhibited thermal diffusivity and compressive strength values comparable with those of commercially available insulators (27 - 0.33 mm^2*s-1 and 2 - 4 MPa, respectively), depending on the amount of fibres. Fractographic analysis evidenced the occurrence of toughening mechanisms such as crack-bridging and pull-out, which contributed to the toughening and strengthening of the material. The fabrication of low-cost masonry materials that can be used either as load-bearing thermal insulator, simultaneously reducing the environmental impact caused by CTs, was thus demonstrated.

Keywords: Silicates, Porous, Composite

ABS 803

THERMOCHROMIC MATERIAL: VANADIUM TITANIUM OXIDE

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Thermochromism is the temperature-dependent change in the color of the material. It could be useful for the monitoring the temperature. This study aims to produce vanadium-titanium oxide, which has a reversible thermochromic property with the green – red color scale.

The synthesis of V_0,48 Ti_0,52 O_2 and V_0,95 Ti_0,05 O were made from vanadyl acetylacetonate and rutile (TiO_2). They were stirred at 150° C for 20 minutes at 300 rpm with the aid of magnetic hotplate stirrer and was placed in a constantly heated furnace (79°C) for solidification. Afterward, both V_0,48 Ti_0,52 O_2 and V_0,95 Ti_0,05 O were placed in the furnace at 500°C for 20 hours.

Their crystal structures, morphologies, and chemical compositions were analyzed with the help of SEM, XRD, and thermal analysis techniques. SEM coupled with EDS technique helped in the determination of inhomogeneities in these compounds where undesired phases may still be existing at some points of the powders.

But this obstacle can be seen as an advantage to produce better dyes with more active thermochromic properties due to their tendency to bond. In the next phase of the study, the color scale of the previously formed powder is intended to be set in green to red instead of brown to red. To convert brown to green, cobalt was used because of its blue color and does not affect the red color when the temperature is increased.

Keywords: Thermochromic Materials, Vanadium Titanium Oxide, Cobalt

ABS 790

DEVELOPMENT OF UV-CURABLE ZrO_2 SLURRIES FOR DIGITAL LIGHT PROCESSING

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Digital Light Processing (DLP) is a powerful technique for the development of ceramic materials with high precision and resolution. The process, in general terms, consists in the polymerization of a photosensitive slurry by the irradiation of light. As the desired part is built layer by layer, any defect as bubbles or agglomerates can difficult the building and sintering processes. Based on that, the development of photosensitive slurries with high homogeneity, stability and reproducibility is necessary.

In this work we present the preparation of UV-curable ZrO2 slurry for its use in DLP. In a first step, the surface of the ZrO2 particles was modified by a dispersing agent, determining the needed amount by zeta potential and particle size measurements. After that, the modified powder was dispersed in an acrylate based slurry, studying the effect of the solid content and the addition of a non-reactive diluent on the viscosity. After the optimization of the printing parameters, the parts were debinded and sintered. Finally, ZrO2 bars were mechanically tested by four point bending measurements.

Keywords: UV curable, Colloidal processing, Digital Light Processing

ABS 782

ROBOCASTING AND RHEOLOGY OF VERY CONCENTRATED ECO-FRIENDLY CERAMIC PASTES

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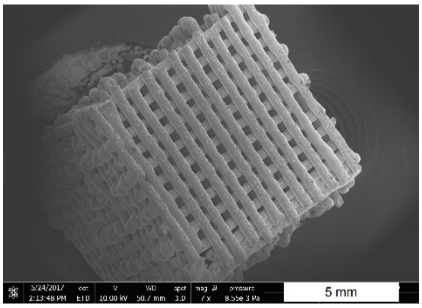
The success of shaping a ceramic product by robocasting depends strongly on the rheological behavior of the used paste(s). However, a correct rheological characterization of pastes is extremely difficult. The relations between the rheological behavior of greater than 45%vol concentrated pastes and the machine parameter settings to obtain a successful printing are not yet completely established. Besides, the rheological behavior of a ceramic mixture depends strongly on its composition. Currently, additives from petrochemical industries are used. To develop innovative materials respecting the criteria of green chemistry, special attention should be paid to water-based solvents and to the use of eco-friendly additives. The aim of this study is then to develop knowledge related to the rheological behavior of eco-friendly ceramic pastes with their aptitude to be extrudable through nozzles of 1 mm to 400 µm.

The aqueous pastes were prepared and formulated with (i) silicate materials, as pastes based on a natural plastic kaolin clay or (ii) alumina mixed with natural additives like psyllium as a binder and lignosulfonate as a dispersant. Their Bingham pseudo-plastic rheological behavior was characterized by flow measurements with a capillary rheometer. This approach is then not sufficient to fully understand their behavior. This is why complementary oscillation measurements and the determination of the limits of plasticity and liquidity are carried out. Thus, without dispersant, the alumina plasticity limit is equal to 20%wt in water whereas with lignosulfonate, it is equal to 15%wt. From oscillation measurements, change in paste behavior (transition from elastic solid state to liquid-viscous state) and the evolution of the rheological behavior as a function of the solid particle amount or over time have been studied. In fact, with good conservation, the pastes can be used for a month.

To shape the ceramic bodies, pastes were extruded with a homemade robocasting device, through a 400 µm or 1 mm diameter nozzle [1]. Different parameters such as the speed value or the use of a pulled back ram and its retraction value were tested. Shaped geometries are 10 mm length scaffolds with a porous grid-like architecture. After consolidation of the ceramic bodies at high temperature, their microstructure was studied by Scanning Electron Microscopy and their density was determined by Archimedes' method.

To conclude, this work demonstrates the possibility of using eco-friendly additives in the preparation of aqueous paste based on alumina or clays. A complete study of their rheology has given an idea of key parameters needed for the feasibility and quality of shaping by robocasting.

The figure below shows a dried alumina scaffold.



[1] J. Bourret and Al., "Micro extrusion of innovative alumina pastes based on aqueous solvent and eco-friendly binder," J. Eur. Ceram. Soc., vol. 38 (7), pp. 2802–2807, 2018.

Keywords: Robocasting, Rheology, Eco-friendly pastes

ABS 781

SYNTHESIS AND CHARACTERIZATION OF AMPHIPHOBIC HYBRID COATINGS FOR INDUSTRIAL APPLICATIONS

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In the coming few years, the control of materials repellence against liquids is one of the biggest challenge to make innovation in many industrial fields. Gathering on the same material the ability of repelling liquids with physical properties (typically surface tension) in a wide range of values represents the topic of many scientific efforts. Materials wetting strictly depends on surface chemistry and reactivity and on structural features at nanoscale as well.

This work is based on the surface modification of aluminum substrates by deposition of thin layers of ceramic oxide nanoparticles, in particular Al_2O_3 and SiO_2 synthesized by sol-gel routes, in order to introduce nano-features which, coupled with the organic modification of the surface chemistry, lead to an almost complete repellence against water (superhydrophobicity, contact angles higher than 160° and contact angle hysteresis <5°) and liquids with surface tension as low as 25 mN/m (superhydrophobicity plus oleophobicity = amphiphobicity). Amphiphobic materials are drawing much interest in different industrial sectors, such as naval, aerospace, energy and automotive, so that great efforts have been making to improve their durability and wearing resistance simulating their application in real environments.

Two different approaches were typically used to produce non-wetting surfaces: the so-called Lotus Leaf (LF) and the Slippery Liquid Infused Porous Surfaces (SLIPS) ones, both introducing textural and chemical modifications at surface level that, in turn, is working in a solid-liquid-air (LF) or liquid-liquid-air three phasic environment. Self-cleaning, anti-icing and anti-soiling behavior was assessed on amphiphobic surfaces and the detected performances correlated to the nature of the coatings, other than to the physical state of the working interfaces.

Keywords: Amphiphobicity, Ceramic nanoparticles, Surface modification, Hybrid coatings

ABS 765

MOLECULAR RECOGNITION AS THE KEY TO SUSTAINABLE PROCESSING OF ELECTRONIC NANOCOMPONENTS

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In the technological field, new outstanding applications require the production of electronics components with increasingly smaller sizes and compatibility with organic media. Flexible electronics, mobile devices and bio-compatible sensor and actuators are the main targets of current research in advanced materials science and technology for high tech applications. The specialized literature evidences an imperative need for new multifunctional materials but keeping an eye on sustainability. In essence, 'nano-manufacturing' is rapidly evolving towards the fabrication of more complex materials in the micro- and nano-scale with precise structure and properties. To date there are some strategies that are able to control the manufacture of these nanoscale components, however, the advances in this field are slow and few mainly due to the difficulty of fabrication processes. Most of the processing techniques involve high cost and energy consuming complex methodologies which require high energy operations in terms of temperature, pressure and/or expensive/ sophisticated equipment. In this frame, the present work chases the sustainable fabrication of self-assembly ZnO-TiO₂ composite by a new approach based on molecular recognition mechanisms and mild processing conditions, i.e, aqueous processes and low temperatures (< 300 ºC). On one hand, the concept of molecular control is used by the binding and assembly of polypeptides to inorganic substrates, a concept used in the field of biomaterials for the development of biosensors, bioreactors, etc. However, up to date, this concept has not been extrapolated to the manufacture of composite materials with a predefined pattern. Molecular control will be combined with methodologies characteristic of the manufacturing, handling and consolidation of inorganic nanoparticles to assemble the building blocks into a defined consolidated shape. The main goal of this work is to achieve the selective immobilization of TiO₂ nanoparticles onto ZnO with nanometric control, using a specifically designed peptide as the linker and link director. At this point, it is important to remark that although this approach could be considered based on biomimetic concepts, no biomimetic structures will be obtained and to the author´s knowledge, this approach has never been intended to grow and re-crystallize oxide nanoparticles into defined solid patterns as the ones needed in microelectronics. The final aim of the work is to extrapolate this new approach to the development of electronic components on a substrate with nanometric control using molecular recognition and soft chemistry processes.

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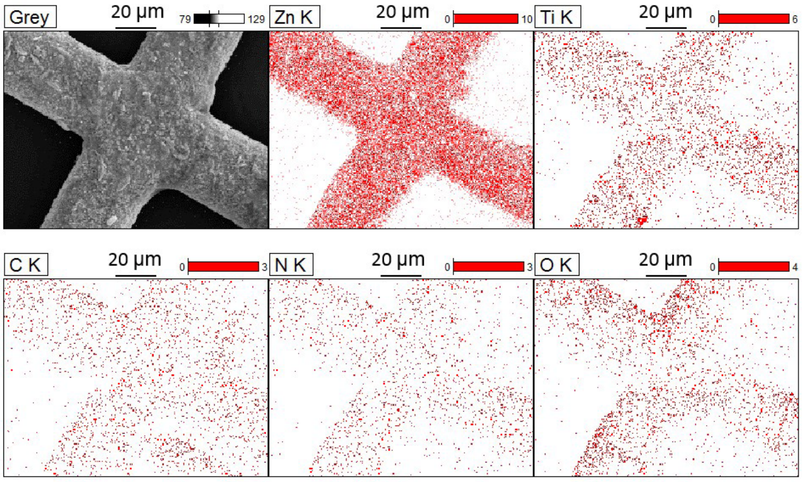
Keywords: Molecular recognition, Functional composites, Nanoparticles



ABS 762

HYBRID NANO-COMPOSITES FOR THE CONSOLIDATION OF EARTHEN MASONRY

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Earth is one of the oldest silicate-based materials in stone heritage, and it is still largely used in architecture worldwide. Adobe bricks are unbaked earth bricks often containing organic fibers and lime, which are commonly used building materials. However, they are highly susceptible to wind and water erosion, leading to loss of cohesion and crumbling. We propose for the first time nano-composites for the surface consolidation of adobe, as conventional consolidants (alkoxysilanes, synthetic or natural polymers) lack physico-chemical compatibility or effectiveness, and can promote degradation.

Mimicking the setting of portland cement, we investigated the formation of calcium silicate hydrate (CSH) within the adobe porosities, owing to the pozzolanic reaction between nanoparticles of silica and calcium hydroxide, to consolidate a powdery substrate. Different formulations were characterized by Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), dynamic light scattering (DLS), and turbidimetry (UV-Vis spectroscopy).

SiO2 nanoparticles, Ca(OH)2 nanoparticles, and hydroxypropyl cellulose were used to formulate a ternary composite, dispersed in a (4:1) ethanol:water blend. Each component is compatible with adobe, and plays a role in its consolidation. The treatment of adobe samples with the composite leads to the in situ formation of CSH, providing resistance to peeling, abrasion, and wet-dry cycles, with no aesthetic alteration. This opens new perpectives in the preservation of one of the most widely used construction materials.

Keywords: calcium silicate hydrate, earthen masonry, hybrid nano-composites

ABS 576

EFFECT OF CALCINATION TEMPERATURE ON THE PRODUCTION OF METASTABLE ZrO_2 NANOPARTICLES PRODUCES FROM SYNTHESIS OF NANOCRYSTALLINE ZIRCONIA USING SOL GEL METHOD

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Nanocrystalline zirconia samples were prepared by sol gel method. Zirconium Propoxide was used as a zirconia precusor. The resulting gel dried in a drying oven at 120 °C for 10 h. All the samples prepared were calcined at different temperatures ranging from 900 to 1100 °C for 2.5 h in a muffle furnace. Samples have predominantly tetragonal crystalline phase but the amount of the tetragonal and monoclinic phases changed as the calcination temperatures were changed. Crystallinity and crystalline phase of zirconia samples after calcination at various temperatures were determined with XRD and the quantitative analysis were done by Rietveld method. Microstructure of the calcined samples were investigated by SEM.

Keywords: zirconia, Nanocrystalline, Sol-Gel

ABS 783

NEW APPLICATIONS OF HYBRID MULTI-MATERIALS AND SMART DESIGN

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Introduction 3D printing lets users push back production limits. Ceramics are no exception to the rule. To open up this technology to a wider spread of professionals 3DCeram is sharing its maker experience to propose smart design (multi-function parts such as 3Doptic system for space application) and multi-material solutions (presentation of the H2020 project Cell3Ditor). Thus, the new Ceramaker Hybrid is able to print several materials at the same time and can manufacture smart design parts.
With 3DCeram Sinto, 3Dprinting is just not repeating what we can do with other production technology but is going a step forward.

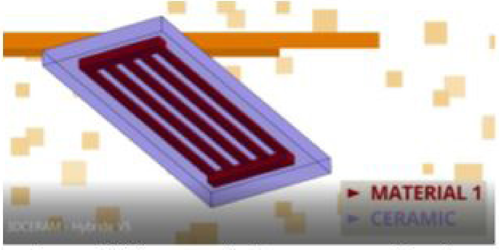
Experimental The principle of hybrid printer is to print in the same time different material and cofired them after. Our hybrid solutions are based on SLA Ceramaker process for the subtract, and another deposit technology for the track or the other material(s). In all cases the objective is to have a compatible system between all materials deposited to have cofired system at the end (compatible ceramic material and solid loading)

We tested:
- Inkjet printing head
- Robocasting for high viscous system (LTCC / HTCC)
- Nozzle jet for low viscous system (SOFC / CORES / FLUIDIC)

During 2018 the study was accentuated on the development of functionalized parts with integrated functions such as internal cannels for fluidic. At the state of the art, with all shaping process for technical ceramics, it is not possible to create parts with long and complex internal cannels.
In order to be able to print such parts the substrate layering (ceramic) was done by SLA (stereolithography) and the internal cannels was created by the deposit of sacrificial resins. This sacrificial resin was deposit by needle valves (nozzles Nordson xQR41) and was polymerized after each deposit in order to solidify the entire part.

Conclusions and discussions After printing, the part is debinded and sintered and by this way the resin deposit in place of internal cannels was burned. After sintering we can obtain pure alumina parts with internal cannels inside. The accuracy of cannels must be qualified

Keywords: stereolithography, hybridation, integrated functions



Drawing of this proof of concept, with alumina in blue, and internal cannels in red

After printing and cutting the part, we can observe the internal cannels made with polymerized resin

ABS 731

FABRICATION OF CERAMIC CORE THROUGH 3D PRINTER AND CONVERTING PROCESS

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Objective The development of 3D printing technology enables the production of precise and complex parts without a separate mold production step. However, in the case of a core prepared through a conventional 3D printer, it is necessary to undergo a sintering process in order to develop the strength, thereby causing dimensional change. Therefore, to solve this problem, an organic-inorganic conversion process was employed as a post process after 3D printing. [1,2].

Materials & Methods Core samples were manufactured using SLS (Selective Laser Sintering) printer and Binder Jet (BJ) printer. In the BJ type, quartz sand of 190 μm and furan resin were cross-stacked to form a green . In the SLS type, phenol resin of RCS (70 μm) was melted to have an adhesive function, and the powder was laminated to form a green . The green was dipped in an inorganic binder solution composed of tetraethyl orthosilicate as a precursor of SiO2 and sodium methoxide as a precursor of Na2O and dried at 80 °C for 1 hour, and then heat treated at 1000 °C for 1 hour to convert the inorganic binder to glass phase.

Results Figure 1(a) shows a high green strength of 40 MPa or more due to the entanglement of the organic binder chain excessively added in the sample. However, the formation of sufficient glass phase was not achieved because of the large amount of organic binder, and the sample completely disintegrated during the heat treatment at 1000 ° C. In the cases of (b) and (c), the strengths of the green bodies before application of the inorganic binder were about 3 MPa. However, when the inorganic binder was applied, the highest firing strength could be obtained in the sample prepared with SLS type printer. This is due to the difference in the shape and size of starting powder. The smaller the particle size, the larger the amount of glass phase can be generated on the surface of particle as the specific surface area increases. As a result, the strength is improved. Actual cores prepared through 3D printers and the post process using the inorganic binder are shown in Fig. 2.

Conclusions A high-strength ceramic core was fabricated by applying an inorganic binder to a ceramic core made by a 3D printer. This study provide a possibility of applying 3D printing technique to prepare a ceramic core in a precision casting.

Keywords: 3D printing, Inorganic binder, converting process

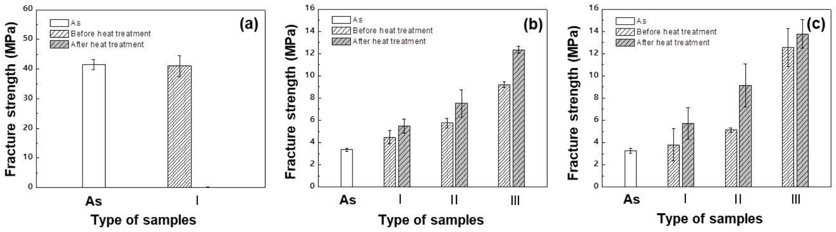

Fig. 1. Fracture strengths of samples prepared using the 3D printer and inorganic binder: (a) BJ type (USA, E company), (b) BJ type (German, V company), and (c) SLS type (Korea, S company).

Fig. 2. Ceramic cores prepared using the 3D printer and inorganic binder: (a) BJ type (USA, E company), (b) BJ type (German, V company), and (c) SLS type (Korea, S company).

ABS 730

POROUS THERMAL INSULATION COATINGS FOR INTERNAL COMBUSTION AUTOMOBILE ENGINES

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Objective In comparison with conventional dense insulation coating, the porous coating can reduce surface temperature of insulation coat on combustion chamber wall rapidly, according with the fluctuating temperature of in-cylinder gas. Therefore, insulation coating with both low thermal conductivity and low volumetric specific heat is useful for heat loss reduction of engine combustion chamber without any sacrifice in other engine performances. For low volumetric specific heat, the coating should be porous. Also, the porous film should have high enough durability – adhesion strength, hardness, and chemical inertness in real operating condition. In this work, we fabricated porous ceramic film with high adhesion strength on engine parts for the purpose of heat-energy management of internal combustion engine.

Materials & Methods Porous ceramic insulation coatings of Y2O3 and ZrSiO4 was deposited on Al alloy substrate by room-temperature operating spray coating process. We use granule for effective delivery of the powder (Granule Spray in Vacuum, GSV). The fine ceramic particles are mixed with the carrier gas and form an aerosol flow, and are accelerated by the pressure difference between the chambers, and ejected through the nozzle with high kinetic energy, then collide with the substrate and form a dense ceramic film without external heating. The ceramic-metal interface had hook-like shape with severely curved interfaces. This anchoring layer makes a strong adhesion of coatings. Density of the films was controlled by changing the kinetic energy and agglomeration of the powder.

Results Y2O3 film with porosity of up to ~23% was fabricated by controlling the powder post-annealing temperature to control the kinetic energy. Porous ZrSiO4 films of 30~60% porosity were made by using ZrSiO4-polyethylene composite powder. The Y2O3 showed better adhesion strength, and the ZrSiO4-polyethylene composite film showed better performance due to higher porosity. Next step we fabricated yttria-zircon composite film to optimize the performance. At the optimum condition, the film showed low thermal conductivity (< 0.5 W/mK), low volumetric heat capacity (< 2000 kJ/m3K), and high adhesion strength (>20 MPa). satisfying the target values from the piston company.

Conclusions Porous and mechanically reliable Y2O3 and ZrSiO4 ceramic insulation coating was successfully fabricated on the internal-combustion engine components. At the optimum coating condition, the film showed good enough mechanical reliability and thermal properties. Therefore, it could be expected that porous ceramic films by GSV would be a potential candidate for insulation coatings of thermal-efficiency management of internal combustion engine.

Keywords: thermal insulation coating, porous film, thermal efficiency

ABS 727

FREEZE-CASTING AS A PROCESSING ROUTE TO FABRICATE ACTIVE MAGNETIC REGENERATORS FOR MAGNETIC REFRIGERATION

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The engineering of directional porosity in the form of lamellar microchannels in ceramics of La0.66Ca0.33-xSrxMn1.05O3 by freeze-casting, or ice-templating, for applications within magnetic refrigeration is presented.

Magnetic refrigeration utilizing the active magnetic regenerator (AMR) cycle offers an alternative to conventional refrigeration using CFC-gasses. The latter poses an environmental risk, while AMR technology is based on a porous magnetic material through which an environmentally friendly fluid flows transferring heat. The efficiency of the AMR cycle strongly depends on the geometry of the regenerator material with an optimal structure consisting of micro-channels while still maintaining a large surface area[1]. Freeze-casting offers a processing route for structures meeting these specific criteria. In freeze-casting, a ceramic suspension is frozen directionally causing a segregation of particles resulting in a two-phase structure of ceramic and ice, where the latter can be removed by sublimation. Under the right conditions, this processing route results in a structure with macro-porosity in the form of parallel, well-defined channels throughout the sample with channel widths of ~10 µm to ~100 µm and solid ceramic walls [2, 3]. We demonstrate how the channel size in this range can be very precisely fine-tuned and kept homogenous throughout a sample using a novel freeze-caster utilizing thermoelectric temperature control with the implementation of various freezing profiles.

The perovskite La0.66Ca0.33-xSrxMn1.05O3 (LCSM) ceramic is well known for its desirable magnetocaloric properties. The Curie temperature can be controlled by varying x [4] making this material ideal for application as an AMR material in magnetic refrigeration [1]. In this presentation we evaluate the performance of AMRs of LCSM fabricated by freeze-casting by estimating heat transfer properties in an oscillating flow test device and measure the achievable temperature span of such regenerators in a versatile AMR test device with a 1.1 T permanent magnet source.

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Keywords: Ice-templating, Porous ceramics, Magnetocaloric cooling

ABS 725

MULLITE HONEYCOMB CERAMICS STRUCTURES MADE BY FUSED DEPOSITION MODELLING (FDM) 3D PRINTING USING PRECERAMIC POLYMERS

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3D printing of light weight mullite honeycomb structures could be succefully demonstrated using Filament Deposition Modeling (FDM) technique. Using FDM printing technology for polymer derived ceramics is new and has not been reported in literature. For lightweight structures, mullite is an interesting material because of its low thermal extension coefficient, high creep resistance, and low density. To obtain mullite, continuous filaments with stoichiometric ratio between the alumina powder and the polysiloxane, and EVA as a thermoplastic binder, were investigated. Three different alumina powder were studied to obtain mullite conversation between 1250 and 1550°C. Using coarse alumina powder, the reaction of mullite did not state at temperatures below 1300°C, while using fine powder revealed in fully cracked pieces after debinding and sintering. A temperature above 1550°C was needed to convert the alumina powder into pure mullite. Morphology of the alumina powder, viscosity of the thermoplastic feedstocks, printing parameters and sintering behavior (SEM, XRD) were investigated to develop the process successfully.

Keywords: Fused deposition modelling, Polymer ceramic, Sintering

ABS 718

SYNTHESIS AND CHARACTERIZATION OF HYBRID NANOCOMPOSITE MEMBRANES FOR CO_2 CAPTION

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In the present work, the elaboration of polymeric membranes from the synthesis of monomers N-3,5-bis (trifluoromethyl) phenyl-norbornen-5,6-dicarboximide and N-pentafluorophenyl-exo-endo-norbornen- 5, is reported. 6-dicarboximide, and its subsequent polymerization, which will be carried out by means of ROMP using the Grubbs Catalyst ™ 2nd Generation, since the aromatic polyimides are materials with an excellent balance of mechanical, chemical and thermal properties that allow their use in the transport and sorption of gases that in this study, the ROMP will be combined to subsequently form dense nanocomposite hybrids (OI) polymer-ceramics with the addition and dispersion nanostructured nanostructured spherical nanocomposite aggregates of TiO2 that were synthesized obtaining a combination of anatase-brookite phases using Tween 20® as a template agent by sol-gel synthesis applying the soft-templating method, via spray-freeze drying and systematically dispersed with ultrasonic sound, to evaluate its potential application as CO2 adsorbents.

The monomers and polymers were characterized by infrared spectroscopy (FT-IR), nuclear magnetic resonance (1 H-NMR, 13 C-NMR, 19 F-NMR), X-ray diffraction, thermomechanical analysis (TMA), thermogravimetric analysis (TGA), Atomic force microscopy (AFM) and mechanical strain-strain tests.

Likewise, nanostructured mesoporous nanocomposite aggregates of TiO2 will be characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, electron microscopy (SEM and TEM), BET analysis and BJH method (Barrett-Joyner -Halenda) to determine the surface area and pore radius respectively.

Subsequently, nanocomposite polymer membranes were prepared by means of an ultrasonic dispersion of different percentages of TiO2 charge, which will be 0.5%, 1% and 2% wt.

To evaluate the functionality of the synthesized materials, functionalization by impregnation of the mesoporous powder was carried out by means of a primary amine and its capture of CO2 was evaluated by thermal analysis (TGA) and in the case of the nanocomposite hybrid membranes, the permeability, selectivity and solubility of the CO2 gas molecule, were also determined.

Keywords: Hybrid Nanocomposites,Hybrid membranes,CO2 caption

ABS 715

ADDITIVE MANUFACTURING OF TRANSPARENT SILICA GLASS FROM SOLUTIONS

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Three dimensional (3D) printing is highly efficient tool, which enables the formation of complex structures that was impossible to fabricate with traditional processes. Although there is a large variety of materials for 3D printings, only few of them can form 3D transparent glass structures.

Fused silica glass is an amorphous material with unique properties such as transparency in a wide spectral range, from UV to the IR, high thermal and chemical stability, high melting point, low thermal expansion, and biological inertness. Conventional processing method for 3D glass structures involves melting or fusing silica particles at high temperatures. The use of particles based inks limits the printability and resolution. Despite the high interest and many potential applications, only few reports on the methods and materials for fabricating 3D glass structures have been published in recent years.

The main goal of this work was to develop particles free ink, which enables printing of 3D transparent glass structure with controlled properties, such as porosity and refractive indices.

Here we present a novel ink for 3D printing of transparent fused silica structures by all-solution ink with a UV-curable sol-gel composition. The developed sol-gel ink obtained by addition of small amount of alkoxide precursors containing UV-curable group to tetraethoxy ortho silicate can be cured before gelation and thus can be printed by localized photopolymerization with the use of a low-cost 3D printer. After the printing, upon aging and densifying, the resulting objects are converted from a gel to a xerogel and then to a fused silica.

By using particle-free ink solution and by controlling the processing steps, we achieved for the first time, the 3D silica structure which remained transparent throughout the post-printing process. The transparency of printed 3D objects with controllable density ranging from 0.8 to 2.2 g/cm3 and refractive index ranging from 1.2 to 1.45 was found to be 92% after final polishing.

Keywords: Fused silica glass, Additive manufacturing, sol-gel ink

ABS 699

HIERARCHICALLY POROUS 3D-PRINTED ÅKERMANITE SCAFFOLDS FROM SILICONES AND ENGINEERED FILLERS

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The research here presented was essentially aimed at producing bioceramic scaffolds, by direct firing of silicone resins with suitable fillers, and with the additional constraint of forming porous struts, that would favour the impregnation with fluids and cell adhesion. More precisely, we referred to highly porous Åkermanite (Ca2MgSi2O7) foams, previously developed from a liquid silicone mixed with CaO and MgO precursors. An intensive foaming was due to simple water vapour release, at 300-350 °C, from the decomposition of Mg(OH)2 and hydrated borate salts, as extra fillers, before firing at 1100 °C. High phase purity could be achieved, with the help of the liquid phase provided by the borate addition (3 wt% of the total ceramic), by reaction of silica, from the silicone polymer, and oxide fillers. A simple update of the silicone allowed for the preparation of silicone-based pastes, comprising CaCO3 (micro) and MgO nano-particles, that were successfully employed for direct ink writing experiments. Despite the change of starting silicone, the phase purity, after firing, was confirmed as excellent. Crack-free scaffolds, with dense and regular struts were achieved by using anhydrous sodium borate (Na2B4O7). On the contrary, scaffolds with homogenous 'spongy' struts were obtained by using hydrated sodium borate. No cracks were observed even in the latter case, owing to water vapour release at low temperature, before ceramic conversion. Both type of scaffolds (with dense or porous struts) exhibited remarkable (crushing strength of 4-7 Mpa with porosity 58-70%) strength-to-density ratios.

Keywords: 3D scaffolds, Polymer-derived ceramics, Direct ink writing

ABS 672

INFLUENCE OF DIVINYLBENZENE ON THE PORE SIZE OF POLYMER DERIVED SiCN CERAMICS

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(Ultra-)Microporous ceramics open new potential fields for ceramic materials, e.g. in environment-related fields such as membrane-based separation, in which both a well-defined and tailorable pore size as well as high stability at elevated temperatures and under harsh conditions are required. Promising materials for these applications are polymer-derived SiCN ceramics, offering superior high temperature properties, and which can exhibit microporosity under certain pyrolysis conditions. For prospective applications it is of great interest to find crucial factors influencing the pore size and stability of these materials during the whole processing chain. Therefore, the use of linker molecules during crosslinking of a commercially available poly(vinyl)silazane on the pore size and specific surface area of the resulting SiCN ceramic was investigated systematically.

A commercially available poly(vinyl)silazane PSZ (Durazane 1800, DurXtreme) was crosslinked via hydrosilylation with different linker molecules, including divinylbenzene (DVB; Sigma Aldrich, 80 %, isomer mixture) and 1,5-hexadiene (HDE; Sigma Aldrich, 97%), using Karstedts catalyst (Sigma Aldrich, Platin(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxan in xylene, ~ 2% Pt). The crosslinked samples were pyrolyzed yielding SiCN(O) ceramics, followed by in-depth characterization including physisorption, small-angle X-ray scattering SAXS, elemental analysis and solid state NMR.

While HDE is burnt out completely without leading to a change in elemental composition or pore size, DVB stays integrated in the network during pyrolysis, leading to a significantly higher carbon content. Physisorption as well as the SAXS investigations showed that DVB has only little effect on the mesoporosity or the overall specific surface area of the resulting amorphous ceramic, but leads to a shift of the micropore size maximum, which is typically found at around 0.8 nm for poly(vinyl)silazane after pyrolysis at 600 °C. The extent of the shift is dependent on the amount of linker molecule, indicating an influence of the aromatic nature of the benzene ring on the bonds in PSZ, thus affecting the pore size in the ceramic. Further information about the bonding types and chemical surroundings of the elements is investigated using e.g. solid state NMR.

The results lead to the assumption that the evolving microporosity is predefined by the cyclic structure of the PSZ, but can still be modified by changing the chemical surroundings. This is an essential finding in order to achieve the applicability and tailorability of the micropore setup of SiCN(O) ceramics for prospective applications as high-temperature membrane materials.

Keywords: Polymer-derived ceramics, Microporosity, Silicon carbonitride

ABS 671

ALTERNATIVE ROUTES TO FABRICATION OF BIOCOMPATIBLE THIN FILM COATINGS ON SHAPE MEMORY ALLOYS

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The development of molecular structures with required physicochemical properties is among the key issues of nanotechnology. There are many challenges related to the nanostructures, especially their influence on the living organisms. In literature, one can find plenty of different methods to manufacture materials in nanometer scale. Each of them may be used to prepare nanostructures with different parameters and properties e.g. powder materials can be used to modification of biomaterials' surface or suitable controlled synthesis procedure may provide production of (nano)coatings, wherein both approaches may be successfully used in biomedical applications. Such coatings behave in a flexible and impermeable way, they are durable as well as homogeneously cover the substrate in entirely surface/volume. As a result, biphasic composites acquire new properties like self-cleaning, catalytic, biological or corrosion protective, etc. However, the key issue remains the choice of appropriate conditions, environmental parameters, and application of high purity reagents.

A problem of manufacturing the suitably biocompatible coatings was tried to solve two-directionally. The first approach was focused on the (1a) chemical co-precipitation method of initial precursors, parameterization of the process, and production of appropriate nanostructures (metallic: silver, copper and calcium phosphates nanoparticles, metallic and ceramic: calcium phosphates, silica oxides nanocomposites) in form of powder. Then, so-prepared powder materials were deposited on the surface of biomaterial (1b) by the electrophoresis, or sol-gel approach providing formation of multifunctional hybrid coatings with different degree of functionality in depending on the type of nanostructures used to surface functionalization. The alternative route was focused on the development (2) of an innovative approach to produce self-assembly structured silica-based coatings based on the mesoporous SBA-15 (Santa Barbara Amorphous) co-deposited at one time on the implantology substrate with calcium phosphate. Coatings developed based on mesoporous silica are characterized by a huge active surface (up to 1000 cm2/g) and might be treated as a potential reservoir for bactericidal substances. Hence, the presence of silica nanochannels (d ~ 2 - 4 nm) located in mesoporous silica occurs that it might be activated by anchoring groups with attached to them biocidal substances, such as silver or copper ions.

Both approaches due to synthesis and materials features give a chance to modify the surface of any biomaterials, not only with a flat surface but very rough, defected or even with an irregular shape. Such coatings improve antimicrobial, pathogenic features, biocompatibility with respect to the human as well as biostimulation, and osteoinductive action.

Keywords: EASA,NiTi, silica-based coatings

ABS 932

ROBOCASTING OF FOLDABLE CERAMICS

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Shaping is one of the more challenging aspects of the fabrication of ceramic parts; with the increasing intricacy of the pieces increases the complexity of green forming. The manufacturing of complex ceramic structures is time, labour and cost intensive. Additive manufacturing technologies have the potential to overcome the limitations of traditional shaping methods such as pressing, plastic and colloidal forming. Robocasting is an additive manufacturing technique that can be used to form green bodies via layer-by-layer extrusion of ceramic pastes. This high-resolution printing method allows for the fabrication of planar structures (both plain and patterned, such as webs) of virtually any ceramic powder as long as it can be used to formulate a printable shear-thinning ink. It cannot, however, on its own produce parts with overhanging features or large unsupported regions.

In this study, a robocasting type has been developed that allows for a combination of printing and post-printing draping/shaping of ceramic parts, both intricate thin nets and test bars. The ink used in the method consists of a ceramic powder dispersed in a highly viscous solution of phenolic resin in methyl ethyl ketone. Printed pre-forms can be folded, moulded over other objects, bended or carved for a certain period of post-printing time defined by the ink composition (solvent content), after which they solidify into final green bodies. Fully shaped parts are then pyrolised and sintered.

Two types of ink compositions have been formulated: one where phenolic resin acts only as a sacrificial dispersion medium (binder and plasticizer) for alumina powder, and another where carbon yielded from the phenolic resin is used as a sintering aid for silicon carbide. Thin nets and bars have been fabricated using both inks and studied for post-printing flexibility and consolidation times. The mechanical properties of the sintered ceramics have been tested using flexural bend test, and the final microstructure assessed via scanning electron microscopy.

Keywords: robocasting, folding, direct write assembly

ABS 649

TAILORING OF THE STABILIZER ADSORPTION ON NANOPARTICLES SURFACES FOR THE NANOSTRUCTURED GROWTH OF CERAMIC COATINGS IN 3D AM STRUCTURES

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Among coating processes, the Electrophoretic Deposition (EPD) have been considered as the most suitable technique for the coverage of complex shapes and additive manufactured porous pieces (i.e. screw, foams or scaffolds) [1,2]. It also show remarkable features comparing with other colloidal techniques, since it allows coating 3D substrates using low concentrated suspension of nanoparticles (NPs), lowering rheology requirements, for growth either porous and dense nanostructured films. Moreover EPD allows producing customized products and reproducing the properties achieved coating 2D substrates in the 3D structures, saving cost in raw materials, as well as reducing process steps following rules of the Green Chemistry.

Understanding the colloidal behavior of NPs is mandatory to prepare stable and disperse suspensions suitable for colloidal coating methods. In electrostatically stabilized suspensions, the morphology, the crystallography and the reactivity of the NPs, determine the charge distribution, while the ionic strength modulates the charge, determining NPs assembly during evaporation. But also, the surface modifiers and suspensions additives are effective tools to manage NPs flocculation and hence ordering. In this work, we will discuss how the Layer-by-Layer (LbL) technology, understood as the alternate absorption of cationic and anionic polymers onto the particle surface, and the control of the polyelectrolyte ionization as well as the suspension ionic strength determines NPs assembly in 3D ceramic coatings by EPD, and hence their properties[3,4].

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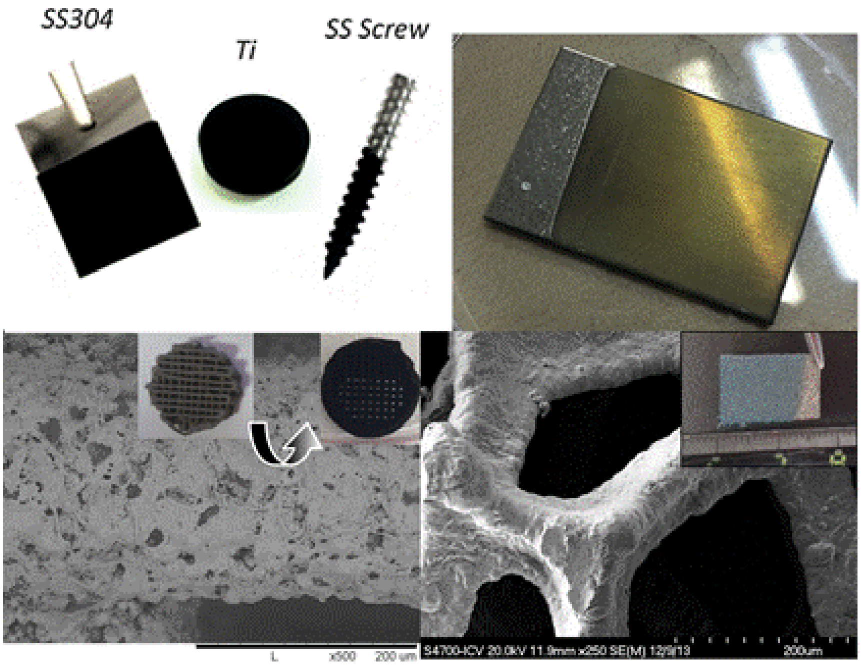
Keywords: Stabilizers, Layer-by-layer, Electrophoretic Deposition



ABS 424

DESIGN OF POROUS CELLULAR Al_2O_3-3YTZ CERAMICS FOR MEMBRANE APPLICATIONS

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Design of the electrochemical cells for alkaline electrolysis aiming hydrogen and oxygen production remains a serious challenge, given by the efficiency of the process, cell size and cost of the components. One possible approach is based on maintaining minimal distance between the electrodes by using a separating membrane between them. The reactivity of alkaline electrolyte and appropriate permeability of the separator to electroactive species impose certain limitations on the range of the materials, which can be used for this purpose. In this scope, a porous membrane of Al2O3-3YTZ was processed with controlled cellular microstructures to be used in the electrochemical process. The processing of the membrane was performed by a recently developed emulsification method of aqueous suspensions of a mixture of Al2O3 and 3YTZ powders in sunflower oil. Taguchi experimental planning was used in order to optimize the experimental conditions of the membrane processing by studying relevant parameters, such as Al2O3 (vol%) content in the mixture of powders suspension (10 vol% to 30 vol%), oil ratio in the emulsification phase (25 vol% to 75 vol%) and firing temperature during a two-step firing approach (1350 °C to 1500 °C, with Delta-T between 50 °C and 150 °C). Combined SEM/EDS/XRD studies were used to assess the microstructural evolution and compositional changes in the cellular membranes. Archimedes method and stereology approach were involved for studying the porosity and the cavity sizes of the cellular structures, respectively. In order to quantify and compare the permeability of such membranes for liquid electrolyte, percolation tests were performed, based on impedance spectroscopy analysis while immersing the membranes in an electrolyte of NaOH (1 M). The two-step firing method was shown to be very effective for consolidation of cellular membranes while maintaining significant open porosity levels between 40% and 58% with the cell cavities linked by a number of interconnecting windows. The results have demonstrated that Al2O3-3YTZ composite cellular ceramics possess appropriate mechanical and chemical stability, and porosity, which can be flexibly designed by the imposed processing conditions, thus being promising as a separation membranes for electrochemical applications.

Keywords: Cellular ceramics, Emulsification, Membrane processing

ABS 643

DIRECT INK WRITING OF NON-OXIDE CERAMICS

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Direct Ink Writing (DIW) is here explored as a way to produce non-oxide ceramic components with different compositions for various technical applications.

The first area of interest is nuclear physics and radiopharmacy: in fact, carbides with specific compositions are suitable for the production of targets in a ISOL (Isotope Separation On-Line) facility and for the emission of radionuclides of medical interest. TiC was selected as target material for the production of Sc radioisotopes. Structures with interconnected pores are desired to minimize impacts between target and isotopes and to allow for effusion; therefore, TiC lattice targets were fabricated from an aqueous suspension with optimized rheology and subsequently sintered without promoting grain growth. Geometries with similar total porosity but different stacking of layers were produced and characterized in order to select a target geometry which maximizes the system performances.

Most applications for non-oxide ceramics, however, require fully dense, monolithic ceramics with good mechanical properties. Further studies were conducted on aqueous suspension of other non-oxide ceramics (SiC and Si3N4) in order to maximize their solid content and the final density of the components. The rheological properties of such inks were characterized and proved suitable for fabricating both porous, unsupported structures and dense components. The deposition process was investigated in order to identify the source of strength limiting defects such as surface roughness and voids at the interface between filaments; particular interest was given to how layers are stacked on top of each other (aligned stacking of filaments, hexagonal build-up, Bouligand structures) and on the surface finish of the samples (as fired or post-processed). Samples properties were characterized and compared with conventional components.

Keywords: direct ink writing, non-oxide ceramics

ABS 627

CERAMIC ADDITIVE MANUFACTURING: A BIBLIOMETRIC ANALYSIS AND EXHAUSTIVE OUTLINE

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Additive Manufacturing (AM) is considered a disruptive technology and the experts think that it is going to shake up the manufacturing industry in the coming years. Since about three decades, AM technologies have been used to fabricate prototypes or models mostly from polymeric or metallic materials. Ceramic materials are, however, not easy to process by AM technologies [1]. In the recent years, various AM technologies are capable of processing ceramic materials have been demonstrated [2], expecting an extraordinary impact on the industrial production with new uses and new markets [1]. With this study, an overview of the history and the tendency of Ceramic AM research is expected to be presented, in addition to the regional particularities, policies, financing efforts and economic growth from the point of view of knowledge production, all of which will be evaluated. Bibliometric analysis is the research area which helps to analyse current trends in the literature regarding a particular area and provides guidelines and motivations for future research work. It basically provides a general outline and overall structure of the research area, and is considered one of the few interdisciplinary research fields that can be extended to almost all scientific fields [3]. Recently, this technique has been used in different research topics such as Big Data [4], Industry 4.0 [5] or Energy [6].

The Web of Science Core Collection (WoS) database was used to search the most relevant scientific articles related to Ceramic Additive Manufacturing. The following main keywords were used for the search: 'Additive Manufacturing' OR '3D printing' OR 'rapid prototyping' and some ceramic keywords to delimited like: ceramic, alumina, glass, cement, zirconia, hydroxyapatite, Al2O3 and TiO2 among others. Only articles and reviews were considered in this analysis, resulting on 2,351 papers published during 28 years.

The preliminary results show that ceramic AM has been gaining a positive exponential growth in the last decades, especially since 2013 (Figure 1), this trend is accordance with the expired patents between 2013-2015 period. Another relevant result comes from the analysis of ceramic AM research by country, showing USA and China as the main contributors to the knowledge development (Figure 2); nevertheless, when considering the whole Europe Union it accounts a considerable higher contribution than USA or China. This reflects the strong efforts produced from the European initiatives towards Additive Manufacturing technologies. Figure 3 reflects the main popular key words used in the WoS database 3 keywords used were rapid prototyping at the beginning (2012), then was 3D printing (2015) and nowadays the keyword used is additive manufacturing (2017) with the surroundings keywords more used as fabrication, mechanical properties, ceramics, scaffolds and hydroxyapatite among others. More specific analysis has been performed showing interesting and promising results.

Keywords: Bibliometric Analysis, Ceramic, Additive Manufacturing

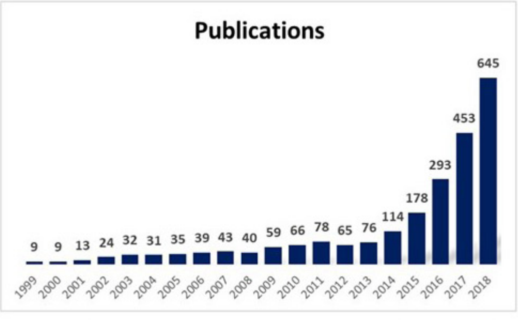

Figure 1 : Number of publications about Additive Manufacturing over the last two decades

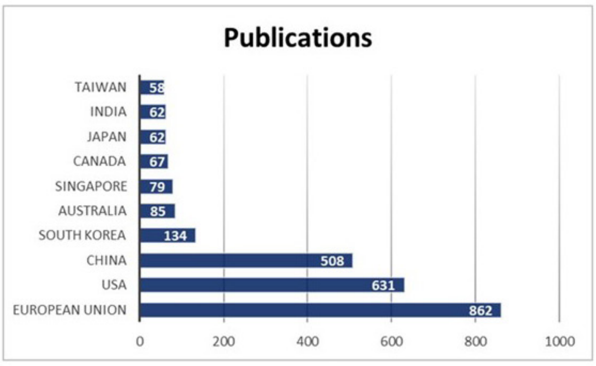

Figure 2. Top 20 countries and EU on Additive Manufacturing research.

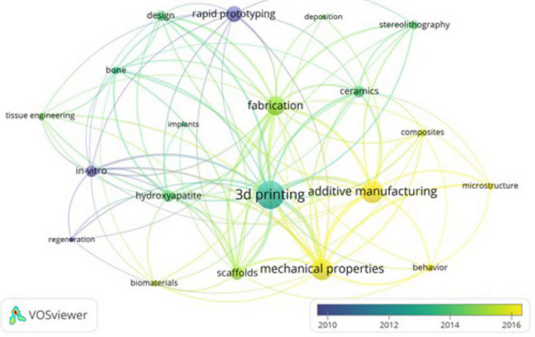

Figure 3: Most popular keywords in WoS

ABS 604

FORMULATION OF CERAMIC RESINS FOR STEREOLITHOGRAPHY-BASED ADDITIVE MANUFACTURING

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Additive manufacturing technologies have expanded the possibilities of ceramic processing. In parallel, their introduction to the market has enabled the discovery of new applications for ceramics. Among all additive technologies, stereolithography-based (SLA) techniques have the most potential because of their high precision and because the final properties of the printed parts are comparable to traditional advanced ceramics. Feedstocks are made by blending ceramic powders with organic resins, generally acrylates. One of the limitations of SLA technologies is to produce slurries with a high solid content while having viscosity under control. The goal is to increase powder solid contents, in order to decrease shrinkage and to improve dimensional stability, while decreasing viscosity. This research presents a chemical approach to make formulations for an improved feedstock handling. A submicron-sized aluminum oxide powder was chosen for this research together with a set of di- and tri-functional acrylate monomers. Moreover, the addition of surfactants was considered in different proportions. It was found that the maximum workable solid content should be in the vicinity of 50 vol% in order to generate a slurry that can be both printed and debound/sintered.

Keywords: Stereolithography, Alumina, Solid content

ABS 603

FABRICATION OF TAILORED STRUCTURES OF SEMICONDUCTORS TiO_2-BASED BY COLLOIDAL PROCESSING

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In the last decades, the design of functional thin films with well-defined nanostructures and the development of novel nanocomposites of semiconductor ceramic-based materials has attracted substantial interest within the scientific community owing to their promising properties, compositions, structures, and functions in a wide range of applications. The TiO2–based materials (coatings, scaffolds, filters, pattern, etc.) with porous microstructures and high specific surface are highly on demand for application involving photoactivity phenomena such as solar cells or photocatalytic degradation. Many attempts to improve the response of the electrodes are based on strategies to induce a better reactant–catalyst contact through the design of complex structures with large surface-to-volume ratio. The structuring and electrochemical activity can be controlled by tuning the physical properties (particle size, crystalline phase, preferred orientation) but also by shaping the TiO2 material host. In this case, the processing of ceramic materials through the use of the colloidal techniques allows nanostructures tailoring, strengthening the control over specific properties. Moreover colloidal chemistry allows the fabrication of specific building blocks such as full inorganic or hybrid core-shell structures that can be shaped in a film.

Those building blocks can be used in Additive Manufacturing (AM) processes, such as Inkjet Printing (IJP) or Fused Deposition Modeling (FDM), to build complex shapes to be economically viable and profitable in industrial applications. 2D or 3D Printing technologies can create patterns and/or pieces using advanced materials in cero-waste process.

In this work, the emphasis is placed on the development of colloidal strategies to tune the microstructure and the geometries of the TiO2 samples. A technological approach based on the use of nanofibrillated cellulose (bioresources from agricultural wastes) as hard template in a hybrid core-shell conformation with TiO2, and/or the use of IJP and FDM are followed to shape advanced and complex TiO2 structures. The suspensions/inks used in the manufacture of samples are previously optimized by colloidal techniques and a post-thermal treatment is occasionally applied to ensure consolidation of the materials. Microstructural properties and photoresponse of the samples will be also presented.

Keywords: Colloidal Processing, Additive Manufacturing, Titanium Dioxide

ABS 601

MULTI-COLOR GRADIENT CERAMICS PRODUCED BY AQUEOUS TAPE CASTING

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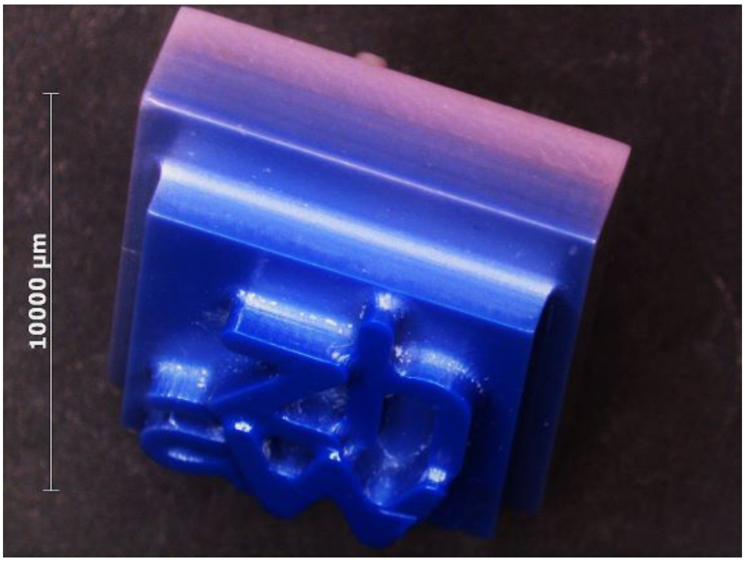
Objective Functionally graded materials find currently an increasing interest, especially in ceramic field, thus broadening the ranges of applications, e.g. for separation membranes, tribological applications, thermal barriers or just esthetic purposes. A general procedure was developed to produce stacks of hundreds of layers with different material properties in such controlled arrangement that smooth macroscopic gradients through the whole block are achieved after firing. As a case study we demonstrate the possibility to create multiple color gradient within ceramic blocks and to machine those to specific shapes.
Materials & Methods Ceramic powders, cellulose and vinyl acetate-based aqueous slurries were used to produce flexible green tapes with thickness ranging from 60 to 200 microns. The fabrication of ceramic blocks followed the stacking up of color tapes at room temperature using low-pressure mold less compaction. Subsequently, the blocks were pre-sintered, and then CNC machined in various shapes and sintered to full density. Scanning electron microscopy, stereo microscopy and UV-Vis spectrophotometry were used to analyze the interior microstructure and gradient color zones.
Results Different prefabricated blocks were shaped by CNC milling and subsequently fired. All ceramics specimens, depending on individual material, achieved relative densities around 99 %. The results from CIE Lab color space coordinates that were calculated from spectrophotometer's reflectance spectra showed high degrees of linearity or reflected the applied material pattern. Results of hardness tests and bending strength were found to be in close match with literature data. There was no significant difference among the perpendicular and parallel layers orientation in stacked blocks.
Conclusions The developed process allows production of functionally graded ceramic materials. As an example, the study shows smooth transitions between color boundaries within ceramic blocks. It can be concluded that process does not negatively affect the mechanical properties and density of ceramic bodies. Furthermore, it provides a more flexible way of creating gradient zone through the ceramics. This makes it a very attractive method, especially for dental applications, but also for other esthetic demands e.g. jewelry and watch industry.

Keywords: Functionally graded materials, Tape casting, Shaping



ABS 600

EFFECT OF STEARIC ACID AMOUNT ON RHEOLOGICAL PROPERTIES OF CERAMIC FEEDSTOCKS FOR FUSED FILAMENT FABRICATION

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Shaping ceramic materials with fused filament fabrication (FFF) still presents a challenge. The main reasons are the unfavorable rheological properties of thermoplastic feedstocks and brittleness of filaments.

Alumina and tricalcium phosphate ceramic feedstocks with ethylene vinyl acetate as a thermoplastic binder and stearic acid as a surfactant were prepared and shaped by commercial 3D printer. Rheological properties and the ability of ceramic feedstocks to be processed into filaments and shaped by the FFF technique were investigated.

The addition of stearic acid effects the viscosity as a function of shear rate in a complex way. Analysis with rheological models show that properties drastically change when the amount of stearic acid surpasses the amount needed for the powder surface coverage. Free stearic acid causes a sudden shift in rheological behavior with a well-expressed yield point. The effect can be advantageous, since yield point improves shape retention during thermal decomposition of the binder. The stearic acid does not only influence the rheological properties, but also the properties of the solidified filament, making it more brittle. Tall structures were printed, debinded and sintered to demonstrate printability, shape stability and excellent fusion between the layers.

Keywords: Additive manufacturing, FDM, Rheology

ABS 593

HYBRID SILICON AND CARBON-BASED POLYMERS: PROCESSING, CHARACTERIZATION AND PROPERTIES

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Partial thermal decomposition of hybrid Si- and C-based polymers allows for unique materials with attractive properties, such as high surface area, high electrical conductivity and pores in nanometer range. Potential applications include gas separation membranes and safer anodes for Li-ion batteries. The system composed of polysiloxane and polycarbosilane polymers as Si-based polymers and divinylbenzene (DVB) as C-based polymer is being explored. Samples composed of polysiloxane and polycarbosilane polymers, with DVB, were pyrolyzed at temperatures ranging from 300 to 800 degrees Celsius at one hundred-degree increments. The weight percent of DVB was increased at 10wt% increments to cover a broad spectrum of Si:C ratio in the final material. In this study the effect of pyrolysis temperature on the resultant material's microstructure and chemistry was investigated by using Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Thermogravimetric Analysis (TGA), BET Surface Area Analysis, and Small Angle X-ray Scattering (SAXS).

Keywords: Polymer Derived Ceramics, Polymer precursors, Hybrid silicon-carbon polymers

ABS 575

PREPARATIONS AND CHARACTERIZATIONS OF LOW-COST POROUS CERAMIC MEMBRANES FOR POTENTIAL MICROFILTRATION AND ULTRAFILTRATION APPLICATIONS

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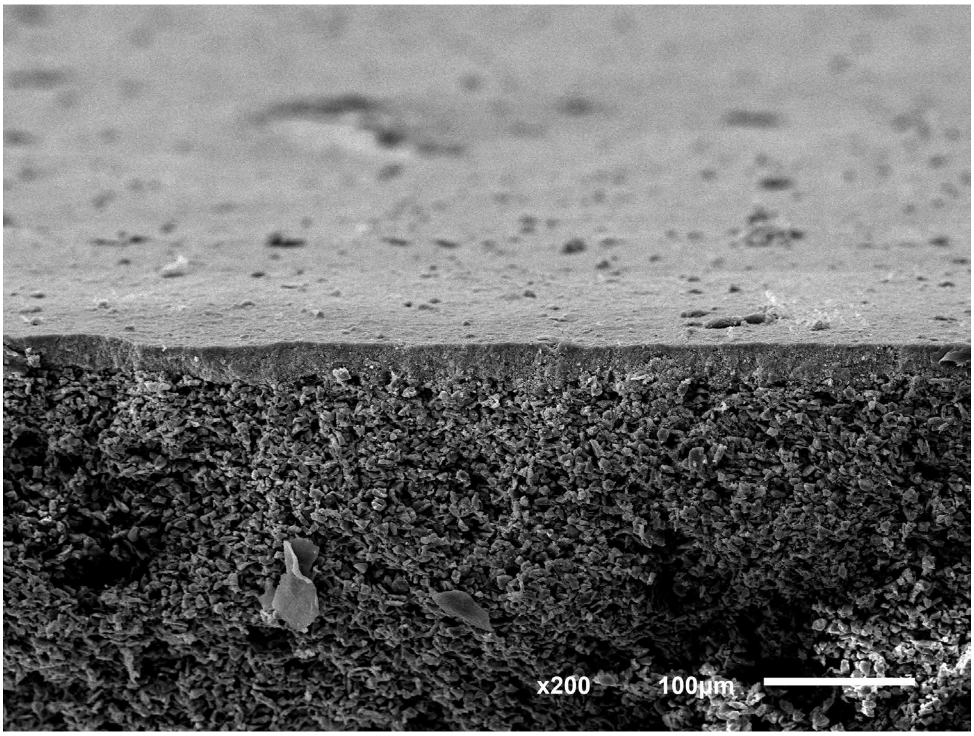
Recently porous ceramic membranes have become a subject of special interest due to their outstanding thermal and chemical stability. To alleviate the manufacturing cost issues of porous ceramic membranes, recent research is focused on the utilization of low cost raw materials. In this study, we introduced porous ceramic membranes prepared from low cost raw materials such as diatomite, kaolin, pyrophyllite, and silicon carbide. And we report the results of our efforts to determine whether we could prepare a low-cost ceramic membranes that could control the average pore size, the largest pore size, the flexural strength and the air/water permeability effectively. The pore characteristics of the specimens were studied by scanning electron micrography, mercury porosimetry, capillary flow porosimetry, and a dead-end microfiltration system with particle counters.

And, in this study, we prepared an alumina-coated low-cost porous ceramic support layer via a dip-coating method with subsequent heat treatment. We reduced the average pore size of a low-cost porous ceramic support layer (1 µm) to 0.1 µm by depositing an alumina coating layer. The thicknesses of the alumina coating layer over a low-cost porous ceramic support layer were controlled via the number of coating layers (from single layer to double layers). The surface roughness of the alumina coating layer was significantly reduced to allow for possible ultrafiltration or nanofiltration applications in future research by introducing a ball-milling process during the alumina coating slurry preparation.

We demonstrated that the water permeability of an alumina-coated low-cost porous ceramic support layer could be reliably maintained during the microfiltration test. We suggest that the alumina-coated low-cost porous ceramic support layer is feasible for water-treatment applications, because a water permeability reduction always occurs after any coating layer deposition, regardless of the type of support layer.

Keywords: porous ceramic membranes, dip-coating process, pore structure control



ABS 572

NOVEL COATING TECHNIQUE FOR PREPARATION OF ALUMINUM NITRIDE THICK FILMS WITH EXCELLENT HEAT DISSIPATION PERFORMANCE

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Objective Aluminum nitride (AlN) has been regarded as an attractive ceramic material applicable to the heat dissipation substrate for high power electronic packages. In the LED and power semiconductor devices, the bulk AlN substrates are typically attached to a metal heatsink via a TIM, which yields a high thermal resistance between the AlN substrates and heatsink due to the low thermal conductivity of polymer-based TIM. In the present study, we tried to make high-quality AlN thick films on an Al substrate by a novel coating technique, without a TIM layer.

Materials & Methods Granule Spray in Vacuum (GSV) process was applied to deposit the AlN thick films on an Al substrate. The AlN granules were prepared by a spray dryer and used as starting materials for deposition. The crystal structure was determined using an X-ray diffractometer (XRD). Scanning electron microscopy (SEM) and transmission electron microscope (TEM) were used to observe the microstructures of the films. The electric breakdown voltages of the films were measured using a withstanding voltage tester (TOS 5101). The thermal diffusivity of the AlN-coated Al substrate was determined at room temperature by the laser flash method using a laser flash unit (LFA 457). Thermal transient measurement of the samples was also carried out with the thermal transient tester (T3Ster) in connection with the DynTIM tester.

Results Aluminum nitride (AlN) thick films (thickness range: 30~100 μm) as a thermally conductive dielectric layer were successfully developed onto an Al substrate using granule spray in vacuum (GSV). The compositions of the starting materials and the resultant films remained unchanged during the coating process. Thermal conductivity values of the films were obtained from the two-layer mode in laser flash analyzer; the values (<11.5W/mK) were much lower than those of bulk ceramics. However, All films showed the excellent dielectric strength (>68kV/mm) and the AlN-coated Al substrate systems exhibited remarkably low thermal resistance, compared to AlN bulk-ceramic system.

Conclusions The GSV coating technique was successfully employed to prepare AlN thick films with thicknesses up to 100 μm. The structure consisting of an AlN thick film and Al substrate exhibited the thermal resistance lower than the commercialized structure which consisted of a bulk-AlN ceramic, a TIM, and an Al substrate, Therefore, it could be expected that AlN thick films by GSV would be a potential candidate as a heatsink for high-power electronic applications.

Keywords: Aluminum nitride, Thick film, Heat dissipation

ABS 569

PROCESSING OF CORDIERITE-MULLITE SUBSTRATES BY TAPE CASTING USING AN ALGERIAN KAOLINITIC CLAY

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The purpose of this work is to study the effect of the sintering temperature on the microstructural evolution, phase composition, and mechanical properties of Algerian clay-magnesite ceramics tapes. A clay deposit of the Tamazert (Jijel, Algeria) was selected for this study thanks to its mineralogical composition and its capacity for industrial use. Different magnesite (MgCO3) content, from 0 to 12 mass%, was added in order to determine the influence over the formation cordierite upon sintering. Tape-casting process was used to produce the green tapes in an aqueous system with optimized amount of dispersant (sodium hexamétaphosphate), binder (PVA 22000) and plasticizer (PEG300). The various green tapes were fired within the temperature range 1000–1200°C for 30 min. In addition, the properties of the green and sintered specimens were characterized using thermal analyses (DTA-TGA and thermodilatometry), X-ray diffraction, scanning electron microscopy, and biaxial flexural strength tests. The results revealed that the clay platelets were mainly aligned along the casting plane and direction, giving rise to textured green tapes. Mullite and cordierite were the main crystallized phases detected in all samples sintered in the temperature range 1000-1200°C. Moreover, as the sintering temperature increased to 1200 °C, the amount of mullite phase increased, and the cordierite phase started to crystallize at 1200 °C. Furthermore, it was found that the biaxial flexural strength values was strongly dependent on the sintering temperature and on the magnesite content. However, the highest flexural strength values (76.9 ± 49 MPa) was obtained for the specimens containing 12 mass% of magnesite and sintered at 1200 °C.

Keywords: Kaolinitic clay, Tape casting, Cordierite-mullite

ABS 564

EFFECT OF SURFACE POLISHING ON THE MECHANICAL PROPERTIES OF CERAMIC PROCESSED BY STEREOLITHOGRAPHY

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It is well known that the mechanical properties of ceramics depend strongly on the finish of the surface. The mechanical properties are determined on cut and polished samples, unlike the final products. In the case of components obtained by additive manufacturing (especially Stereolithography-SLA), post-processing and finishing is a difficult task which cannot usually be performed for very complex parts.

The objectives of this work are to determine whether or not the finish of the surface of raw parts obtained using SLA has an impact on the mechanical properties. SLA specimens were prepared, sintered and further characterized by 3-point bending tests. A comparison of the mechanical properties was performed between raw and polished samples. Moreover, mechanical strength of specimens processed by a classical shaping route (powder pressing) has been determined as well for completeness.

The European Regional Development Fund (ERDF) and Wallonia, are gratefully acknowledged for their financial support to these research projects CERAMTOP and CERAMPLUS “Iawatha” in the frame of the “Transition programme.”

Keywords: stereolithography, Flexural strength, Roughness effect

ABS 555

MECHANICAL CHARACTERIZATION AND ISOTROPY OF CERAMICS PRODUCED BY ADDITIVE MANUFACTURING

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Additive manufacturing (AM) techniques increasingly become a relevant fabrication method in the field of high-performance ceramics. The increasing importance of these components also requires the availability of testing procedures that ensure the quality and homogeneity of parts made by AM.

Using alumina as a model system, in this contribution we present mechanical properties obtained on specimens from additive manufactured alumina components. Specimens tested in different orientations with respect to the building direction are investigated. The relation between the applied stress direction, strength and building direction is presented. The obtained mechanical data is correlated with a microstructural investigation based on light microscopy and scanning electron microscopy to give more insight into the structure-property relationships.

Mechanical and fractographical data show that there is a strong impact of the process conditions on the obtained material properties, especially concerning the printing parameters and the applied sintering conditions. For the alumina model system, a mechanical strength of more than 400 MPa could be realized. For machined parts (grinding and polishing) the effect of the printing orientation became negligible and the microstructure, as well as the material properties, were homogeneous throughout the part. For parts tested in as-fired condition without further machining, an impact of the printing orientation could be detected. By optimizing the printing parameters and conditions this effect could be minimized.

It is shown that proper choice of the materials as well as the printing and post-processing parameters are extremely important to realize a homogeneous and isotropic microstructure and thus, ceramic components with isotropic material properties. If everything is done correctly it is possible to realize homogeneous and isotropic components with a performance on eye-level to traditionally manufactured ceramics. Nonetheless, these findings also demonstrate that for 3D printed parts the use of common and accepted testing protocols is crucial to be able to provide reliable data.

Keywords: stereolithography, mechanical characterization, alumina

ABS 540

FREEZE CASTING OF HIGHLY-POROUS γ-Al_2O_3 FOAMS

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The objective of this work was to prepare highly-porous γ-Al2O3 ceramic foams with hierarchical heterogeneities, high specific surface areas and permeabilites, aimed at applications such as thermal insulation, adsorption, catalysis. For this purpose, freeze casting was chosen as a simple but efficient technique for consolidation of aqueous suspensions containing mesocrystalline γ-Al2O3 2D nanosheet-like particles, hierarchically assembled into globular, micron-sized entities. The effect of dispersant, divalent cations and/or cellulose nanofibers addition on the suspension stabilisation, rheological properties and freeze casting behaviour were studied in detail.

Abundant amounts of γ-AlOOH powder were prepared by exploiting the aluminium nitride (AlN) powder hydrolysis [1] as a straightforward and pure method not requiring any surface directing agents nor hydrothermal steps. After calcination the topotactically transformed γ-Al2O3 powder was dispersed in water and the suspensions were characterised for the zeta potential, sedimentation, and rheological properties. The suspensions were shaped into foams via unidirectional freezing at different cooling rates and subsequent freeze drying. The foams were analysed for pore size distribution, specific surface area, thermal conductivity and compressive strength.

The freeze casted γ-Al2O3 foams showed low relative densities (2.3-8.9%) with hierarchically distributed pores. Larger, macro pores (1-100µm) were introduced by ice growth during freezing process. The smaller, mesopores (4-7 nm) that were present in the foams struts originated from the mesocrystalline nature of the assembled nanosheets of the starting powder, which also contributed to the foams high surface areas (~160 m2/g) and lowered thermal conductivities (0.08-0.18 W/mK). Besides foams exhibited high rigidness rarely seen in green bodies with such high porosities.

Keywords: gamma Al2O3,suspension characterization, freeze casting

ABS 531

NOVEL PHOTORESPONSIVE SLURRY SYSTEM DESIGNED BY TAILOR-MADE FUNCTIONAL DISPERSANTS FOR COMPLEX SHAPED AND RAPID DEWAXABLE GREEN COMPACTS

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A new photoresponsive slurry system which can be applied to shaping complex structured green compacts by gel-casting and/or micro-scaled stereolithographic technique and further processable into rapid dewaxing/sintering without forming cracks has been successfully designed. Using spherical silica nanoparticles as a model study, the photoresponsive slurry was designed by adding small amount of multifunctional acrylates (MA) and photo radical initiators into dense silica nanoparticle/nonaqueous solvent slurry stabilized by a tailor-made functional dispersant; polyethyleneimine complexed with oleic acid (PEI-OA) in various PEI:OA ratios. The UV light irradiation to the slurry caused the polymerization of MA followed by the polymerization heat induced Michael additive reaction between polymerized acrylates and amine groups of PEI-OA on silica nanoparticles. The interparticle network formation by small amount of organics resulted to successful sight-selective solidification of the slurry induced by UV light irradiation. Furthermore, the dispersion stability of designed slurry and their solidification properties were able to be controlled by tuning the PEI:OA ratio of tailor-made functional dispersant. Using the designed photoresponsive slurry system, a complex structured green compacts were fabricated through gel-casting process and/or micro-scaled stereolithographic technique. Since the total organic content in the slurry was quite low, the fabricated green compacts were able to be dewaxed without conducting slow heating profiles. Heating the complex shaped silica green compacts at 1623 K (5 K/min.) resulted to transparent sintered material maintaining the apparent shape of green compacts.

Keywords: Photoresponsive slurry, Functional dispersants, Rapid dewaxing

ABS 1

INNOVATIVE FORMING PROCESS FOR 3Y-TZP MICROSPHERES BY THE USE OF INKJET-TECHNOLOGY

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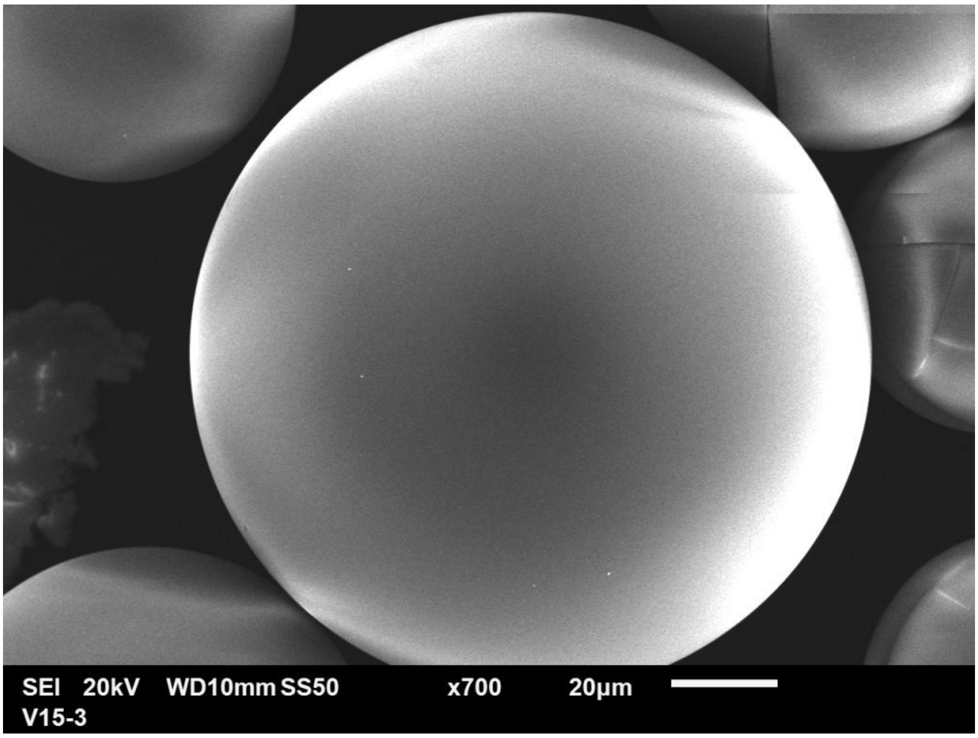
The use of microspheres with a diameter of < 100 µm is of great importance in numerous applications for example grinding and dispersing technologies. The article presents the development of a manufacturing process by combining the sol-gel technology and the specially developed and patented inkjet dropping technique for the production of microspheres from 3Y-TZP. The newly developed process technology allows the production of uniform microspheres in a continuous manufacturing process. The contribution deals with the main influencing factors in the production of microspheres and presents the latest development results.

Keywords: Microspheres, SolGel, InkJet



ABS 508

PROGRESS IN MANUFACTURING AND EVALUATION OF CHEMICAL PROPERTIES OF OXYGEN-BUFFERED UO_2 FUELS, USING SOLID REDOX BUFFERS

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Under off-normal operating conditions of Nuclear reactor, the fuel UO2 undergoes high thermal and mechanical stresses giving rise to a significant release of fission products, of which some, like iodine, may be corrosive towards the zirconium cladding.

The release of volatile fission products, The release of volatile fission products, such as Cs, I or Te in the composition range of irradiated nuclear fuels, is thus governed by coupled thermo-chemical-mechanical processes. Temperature and O2 partial pressure are actually the main parameters controlling the speciation - and consequently the corrosive or non-corrosive character - of volatile fission products (other than rare gases).

In order to limit the risk of cladding corrosion and to improve the performance of the reactor, one possible solution consists therefore in designing an oxygen-buffered UO2 fuel, which would stabilize the non-corrosive CsI species under operation instead of the actual corrosive form TeI2.

In this study, the ability of solid redox buffers incorporated in UO2 for controlling the in-situ O2 partial pressure of the fuel - and thus the speciation of volatile fission products - is evaluated. Two redox buffers, (Mo/MoO2) and (NbO2/Nb2O5), which are expected to stabilize the species TeI2 for the former and the species CsI for the later, are compared.

A manufacturing process of UO2 pellets doped with a redox buffer was optimized. A specific laboratory device was designed in order to preserve both oxido-reducing forms of the oxygen buffer in the pellets while sintering. It is composed of a quasi-closed vessel, in which were placed side by side the UO2 pellets to sinter and a redox buffer, under powdered form, of same nature as that incorporated in the pellets. Under these experimental conditions, the sintering was carried out under a strictly controlled O2 partial pressure, with no modification of the buffer systems incorporated in the pellets. The methodology was validated by determining the speciation of molybdenum and niobium after sintering in both solid solution and solid phases using and Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD).

The paper will summarize the progress in manufacturing process of UO2 pellets doped with a redox buffer and evaluation of chemical properties of oxygen-buffered UO2 fuels, using solid redox buffers.

Keywords: UO2 pellets, Buffer couple, sintering

ABS 504

SOLUTION COMBUSTION SYNTHESIS AS A POWERFUL TOOL FOR PREPARATION OF NANOMATERIALS OF DIFFERENT FUNCTIONAL CLASSES

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Objective The main goal of the research work was to develop fast, cheap, multifunctional and easy scalable method for synthesis of inorganic nanomaterials (ceramics, metals and cerametallic complex compositions) of different functional classes like phosphors, abrasives, catalysts, electrodes for supercapacitors and batteries etc.

Materials & Methods To synthesize all the materials modified solution combustion synthesis (SCS) method was used. In general case stoichiometric amounts of metal nitrates as metal-ion sources/oxidizer and organic fuels (urea ($CH4N2O$, U), citric acid hydrate ($C6H8O7·H2O$, CA), glycine ($C2H5NO2$, G), and hexamethylenetetramine ($C6H12N4$, HMT)) as reductants were used to prepare water-based solutions, containing all required compounds. Then solutions were dried and burned to obtain final nanopowders. After that prepared nanopowders were used during following technological stages as they were or for fabrication devices (sensors, electrodes and catalysts) and functional coatings (abrasives, catalysts, corrosion protecting coatings etc.).

Results In the results of the research universal and scalable approach for nanomaterials synthesis was developed and inorganic ceramic, metallic and cerametallic nanomaterials of different functional classes were successfully obtained, characterized and practically used. For example, ferroelectric and multiferroic nanoceramics base on RE-doped $BaTiO3$ and $BiFeO3$ were synthesized and used for fabrication of energy efficient semiconductor $CO2$ gas sensor. Cerametallic carbon@$Fe2O3$ composite and alumina-cobalt ferrite composites were used as highly efficient catalysts for water deironing and fabrication of carbon nanotubes, respectively. There were synthesized nanopowders of pure metals (Co, Cu, Ni) and high entropy allows. Finally, conditions for creation of an industrial plant for the synthesis of inorganic ceramic, metallic and cerametallic nanomaterials by continuous solution combustion method were developed.

Conclusions Modified solution combustion method for fast, easy and cheap synthesis of inorganic ceramic, metallic and cerametallic composite multifunctional nanomaterials was successfully developed and used. The method became a powerful and universal tool, which can be used in multiply cases for nanomaterials synthesis and can be easy scalable for high productive industrial plants.

Keywords: solution combustion synthesis, nanopowders

ABS 481

THERMAL AND MECHANIC PROPERTIES OF ALUMINUM TITANATE OBTAINED BY MEANS OF HETEROGENEOUS NUCLEATION

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Tialite is synthetic refractory material with Al2TiO5 structural formula. The biggest limitation in the potential use of tialite as a refractory material is its thermal instability within the range of 750-1280°C. It was found that the magnesium oxide and silicon oxide introduced into the system in the small amounts effectively limit the decomposition of tialite. MgTi2O5 is one of isostructural with tialite, transitions phase occurring during the synthesis. Therefore it is possible to synthesize tialite by introducing into the reaction mixture seeds of MgTi2O5. Forming of tialite solid solutions with general formula MgxAl2(1-x)Ti1+xO5 should result in lowered temperature of the synthesis, and an increased thermal stability.

The presented results compare two methods of tialite synthesis such as: 1) solid state reaction synthesis using magnesium titanate in-situ synthesis and 2) heterogeneous nucleation with the use of isostructural phases in the form of magnesium titanate. The synthesis was carried out on samples varying in quantity and type of used additives. Yield of synthesis reaction was specified by XRD method. The bending strength was determined by a three-point bending method. Thermal expansion of individual systems and their thermal conductivity coefficient were investigated. Moreover, the influence of the composition of the initial powders on the thermal stability of the finished products was determined. Resistance to thermal shock of the following products has been measured. The obtained materials were characterized by improved thermal stability and better mechanical parameters in relation to pure tialite, with a slight decrease in thermal properties (increase in thermal conductivity coefficient, slight decrease in thermal shock resistance).

Acknowledgements
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Keywords: tialite, heterogenic nucleation, thermal expansion coefficient

ABS 476

SYNTHESIS OF B_4C POWDERS FROM MONO- AND POLYSACCHARIDES

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Boron carbide, in a form of dense polycrystals, can be usually applied as a structural material e.g. as cutting tools, grinding media, milliners, elements of anti-ballistic shield or nozzles for sandblasting and water cutting. The high cross-section in relation to neutrons allows using of boron carbide powders and polycrystals as boron carrier in the boron-neutron therapy or as shielding elements in the nuclear industry. There are few methods of synthesis of boron carbide powders and the most commonly used one is a carbothermal reduction of boron compounds usually boric acid or directly boron oxide. The source of carbon is such synthesis can be fine crystalline graphite or coke oil. Recently, there are developed of some methods of boron-carbide-powders synthesis by means thermal decomposition of solid precursors formed by evaporation of water solution containing a well-soluble organic compound and boric acid. For example, decomposition of precursors made from solutions of boric acid and citric acid or glycerin, oxide boron and amorphous carbon were obtained, where carbide boron was synthesized already at 1500-1600°C.
The aim of this work was a synthesis pure powders of boron carbide using boron acid and monosaccharides (fructose, glucose) or polysaccharides (dextrin, hydroxyethyl starch - HES) as a source of carbon. Respective weights of boric acid and mono- or polysaccharides were dissolved in distilled water in proportions giving boron to carbon ratio in the final powder of 1 to 10. The solutions were dried overnight at 120°C to form of viscous resin and then pyrolyzed at 850°C for 1h. The powders were ground in SiC mortar and heat-treated at a temperature range of 1300 - 1700°C for 30 half an hour in an argon atmosphere.
Infrared spectroscopy analysis revealed that the addition of boric acid changes of a saccharide structure, some new bands that can be attributed to different B-O and B-O-C bonds in the respective spectra was visible. Similarly, Raman spectra of the pyrolyzed samples showed the presence of a different form of carbon. It was stated, that synthesis of boron carbide started at 1300°C and the reaction between boron oxide and carbon proceed with temperature. Microscopy observations indicated that morphology of boron carbide particles depended on the synthesis temperature and strongly depended on used saccharide.

The part of this study was supported by the NAWA (Grant Nr. PPI/PRO /2018/1/00026).

Keywords: boron carbide, saccharides, powder synthesis

ABS 460

PREPARATION OF UO$_2$ - PuO$_2$ MOX FUEL BY TWO INNOVATIVE WET PROCESSES: FREEZE GRANULATION AND SLIP CASTING

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Objectives The production of MOX (UO2-PuO2 nuclear fuels) is currently carried out by a dry process, involving steps with fine powders (grinding, mixing, pressing). In order to limit dust dissemination in glove boxes and have a better U-Pu homogeneity in the final material, new wet processes are investigated.
Materials & methods The key step of these wet processes is the preparation of a stable and well-dispersed aqueous UO2-PuO2 suspension through the use of an appropriate wet-mixing process and an optimized amount of proper dispersant, in order to have a charged, yet fluid, homogenous and settling-resistant suspension. Two different liquid processes are intended from these suspensions:
- freeze granulation (Fig. 1): the suspension is atomized in liquid nitrogen. Suspension droplets freeze instantly into frozen granules, which are eventually freeze-dried to yield a granulated powder. Granules are shaped into pellets by uniaxial pressing [1].
- slip casting (Fig. 2): the suspension is poured into a porous mold. Its porosity extracts the water from the suspension by capillarity, eventually forming a green pellet.

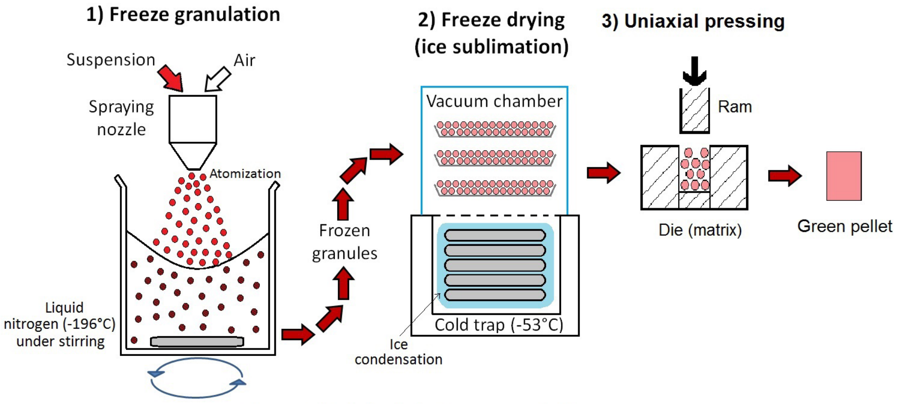

Fig. 1: Principle of the freeze-granulation process.

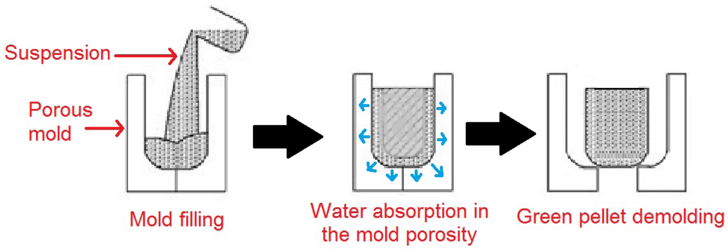

Fig. 2: Principle of the slip casting process.

Results The use of grinding balls and roller mixer has proven to be an efficient way to prepare charged (30-35 %v solid loading, i.e. 80-85 wt%) UO2-PuO2 aqueous suspensions, in combination with polymethacrylate dispersant. These suspensions exhibit good dispersion (assessed by acoustophorometry through the measurement of zeta potential) and settling resistance, despite the materials high density (around 11 g/cm3 for UO2 and PuO2). Rheology measurements showed that the suspension viscosity was low enough to allow atomization. From these optimized suspensions, MOX pellets were formed by the two aforementioned processes. Their sintering behavior and microstructure were characterized in detail.

Conclusions Two liquid route processes, slip casting and freeze granulation, were applied to the preparation of MOX pellets from raw UO2 and PuO2 powders. Their advantages upon the industrial dry process are: lower dusting and better pellet homogeneity. The key step of these wet processes is the suspension preparation, which properties are bound to rheology and colloidal chemistry considerations.

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Keywords: freeze granulation, suspension, slip casting

ABS 455

THE SILICA ADDITIVE INFLUENCE ON THE DENSIFICATION BEHAVIOR AND MASS TRANSFER MECHANISMS IN 3Y-TZP NANOPOWDERS

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For the improving of mechanical and physical properties of zirconia ceramic materials such as strength and hardness, ionic conductivity, biocompatibility, usually use different physical and chemical treatments. In the present study both mechanical activation and chemical treatments were used for the 3Y-TZP nanopowders structure modification and the impact of this modification on the initial sintering stage has been investigated. It was found that silica addition led to the dominant sintering mechanism changing in 3Y-TZP at the initial sintering stage.

The 3Y-TZP-SiO2 nanopowders structure with different amount of silica (0.2-10 wt%) and its sintering behavior have been investigated. It was found that silica additive caused the dominant sintering mechanism changing from volume diffusion mechanism to grain boundary diffusion and to the volume diffusion with viscous flow mechanism participation with silica amount increasing up to 10 wt% in powders obtained by co-precipitation. As for the powders 3Y-TZP-SiO2 obtained by mechanical mixing the mass transfer mechanisms changing occurs in a different way due to the mechanical activation influence. The dominant sintering mechanism changes from grain boundary to the volume diffusion with viscous flow mechanism.

Thus, such a sintering mechanisms changing in 3Y-TZP doped by silica caused the densification acceleration and activation of consolidation because the activation energy of sintering was decreased in both types of investigated 3Y-TZP-SiO2 nanopowders.

Keywords: Zirconia nanopowders, Additives, Sintering

ABS 432

PRESENCE OF AMORPHOUS SILICA DURING SYNTHESIS OF CORDIERITE IN THE KAOLINITE-TALC-ALUMINA SYSTEM

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The amorphous SiO2 released before the formation of Al-Si spinel from kaolinite during synthesis of cordierite in the Kaolinite-Talc-Alumina system was examined using DTA, FTIR and XRD techniques.

The amorphous SiO2 may affect the formation of transition phases during the process of cordierite synthesis. Kaolinite powders release amorphous SiO2 when heating at temperature above 700 degrees Celsius. The temperature range for SiO2 release varies with the particle sizes of powders. Three 700 degrees Celsius-calcined kaolinite powders of particle sizes d50=386, 641 and 1104nm were mixed well with powders of talc (d50=900nm) and alumina (d50=220nm), respectively in stoichiometric composition of cordierite. In the K-T-A system, the amorphous SiO2 release from calcined kaolinite was the main observation object. The temperature ranges of amorphous SiO2 were investigated by DTA techniques. The calcined kaolinite powders then were thermally treated at the temperatures selected from the temperature ranges of SiO2 release as observed by DTA measurements. The shift of Si-O stretching of the released SiO2 was evaluated using the thermal-treated samples, by FTIR techniques at the region 1300-1000 cm-1. The presence of transition phases in the corresponding samples was identified by XRD techniques.

It is found the amorphous SiO2 released from the 700 degrees Celsius-calcined kaolinite powders significantly affects the low-cordierite formation during cordierite synthesis. The calcined kaolinite with finer particle sizes will show a narrowed but clearer hump on DTA profiles of temperature ranges during SiO2 releasing. FTIR investigation also demonstrates that the narrowed temperature ranges are normally accompanied with the shift of Si-O stretching to higher wavenumbers that is more apparent, indicating an increase in SiO2 release. This can provide a SiO2-rich synthesis condition. Thus, low-cordierite can be formed abundantly within a shorter duration at lower temperatures, 1050 degrees Celsius.

Keywords: Calcined kaolinite, Amorphous SiO2,Cordierite

ABS 421

MESOPOROUS (HYBRID) SILICA NANOCHANNEL MEMBRANE

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Many industrial process streams contain solvents or water/solvent mixtures and other valuable components what needs to be separated. Polymeric nanofiltration membranes nowadays widely used in wastewater and water treatment normally show good permeability and stable rejection. They offer a more sustainable and energy efficient alternative to currently used separation technologies. However, these good performances are often lost when the mixture contains a solvent due to phenomena like swelling and membrane degradation. We have developed a mesoporous (hybrid) silica nanochannel membrane (SNM) directly on top of a porous ceramic support via a basic sol-gel emulsion route. The effect of different parameters, e.g. reaction time and reaction volume, on the formation and morphology of the membrane were studied. The first results show a thin defect-free layer (~50 nm) on top of a γ-alumina intermediate layer (Figure 1). An important increase of the water permeability was observed from 0.9 to at least 3.6 L m 2 h 1 bar 1 as compared to the standard Evaporation Induced Self Assembly (EISA) method (Figure 2). The increase in flux suggests that there is an improved alinement of the pores and currently the nanochannels orientation is examined by GISAXS. This novel membrane is a very interesting material for solvent filtration, and at the present time we are applying this method to develop hybrid mesoporous silica nanochannel membrane (HSNM) what could be used for separation of valuable components from water/solvent mixtures.

Keywords: Nanochannel membrane, Mesoporous silica, Hybrid material

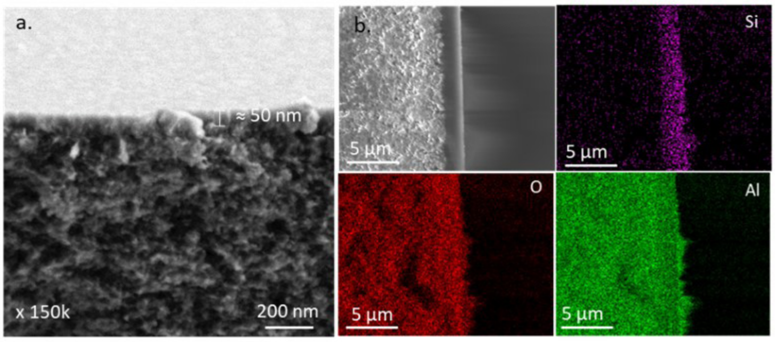

Figure 1: Cross-sectional FE-SEM images of the mesoporous silica membrane (a.) and the corresponding EDX maps (b.). The violet, red and green dots represent the concentration of Si, O, and Al atoms respectively.

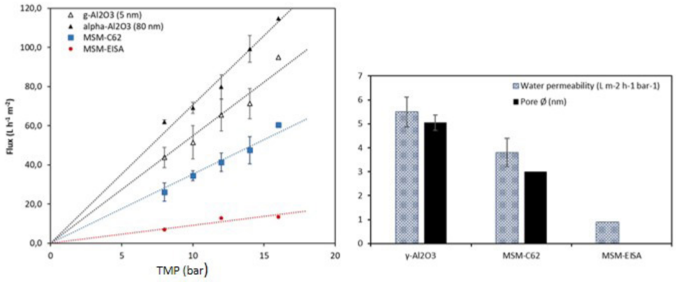

Figure 2: Left, flux vs. trans membrane pressure (TMP) of different membranes. Right, pore diameters and water permeabilities of γ-Al_2O_3 and mesoporous silica membranes. Pore diameter was deduced from the permporometry analysis, the pore size of MSM-EISA was below the detection limit (1,5nm).

ABS 418

ADDITIVE MANUFACTURING OF PORCELAIN AND ALUMINA BY LSD-PRINT

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Powder-based additive manufacturing processes are popular in the field of additive manufacturing of metal parts. One reason is the higher productivity compared to other technologies. For ceramic materials, powder based additive manufacturing technologies often results in porous ceramic parts. The layerwise slurry deposition (LSD) technology unites the advantages of a powder-based process regarding productivity with the possibility to produce dense ceramic parts like it is possible with stereolithography. This is achieved by a high packing density of the powder bed and consequently a high green density. We will present the LSD-technology to produce porcelain and alumina parts. Green bodies and sintered parts will be shown. Their properties are equivalent to conventionally produced parts. Their microstructure and mechanical properties will be discussed.

Keywords: Layerwise slurry deposition, alumina, porcelain

ABS 409

ROBOCASTING OF DENSE CERAMIC SINGLE- AND BI-MATERIALS WITH COMPLEX GEOMETRIES

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Additive manufacturing of ceramic materials has been rapidly expanding for several years. Robocasting (sometimes referred as Direct Ink Writing) is one the few additive manufacturing technologies that would allow processing with the same technology multi-materials. Robocasting uses mechanical forces to extrude ceramic pastes (called « inks ») from one of several syringes through thin nozzles, following a computer-aided design model to form green 3D structures. Robocasting has been used successfully to produce porous, architecture scaffolds. Our goal is here to use the robocasting to print dense 3D-structures with complex geometries such as cones or spheres, made of either a single material or bi-materials (zirconia and alumina). Two sets of parameters were studied in our work to reach this goal, related to both the ceramic pastes and the printing parameters. Optimization of the ceramic pastes aims at two main goals : reaching optimal rheological behavior and obtaining perfectly homogeneous pastes. Indeed, to allow extrusion through fine nozzles, agglomerates and bubbles should be removed and a homogenous ceramic paste must be obtained. The rheological properties are also considered to be one of the most important factors for a successful printing. Therefore inks properties were evaluated in terms of viscoelastic behavior (i.e. yield stress, shear-thinning behavior, viscosity, stiffness). Both homogeneity and rheology can be optimized by the formulation of ceramics paste, in particular with a work on the optimum amount of dispersant and gelling agent (here, Alginate or Pluronic F127), and an optimization of mixing sequence. In addition, the influence of printing parameters was also studied : path of the nozzle to make the design, use of two syringes to create either support structures or bi-materials architectures, etc. Printed parts were characterized Scanning Electron Microscopy and X-Ray Tomography at each stage of the process (after printing, debinding and sintering).

This work is a part of the CERAPID ANR project, supported by the French « Agence Nationale de la Recherche » under grant number ANR-17-CE08-0021, and that brings together SIMAP (Grenobles), LGF (St Etienne), CRISMAT (Caen) and MATEIS (Lyon) laboratories.

Keywords: robocasting, direct ink writing, complex shapes

ABS 401

COMPLEX-SHAPED SILICON CARBIDE CERAMIC PARTS PRODUCED BY PELLETS ADDITIVE MANUFACTURING AND REACTIVE MELT INFILTRATION

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Additive manufacturing (AM, also called 3D printing or rapid prototyping) offers the possibility to produce complex shaped structural parts and to have customized, small and fast production series.

Using the advantage of the high maturity technology level of thermoplastic AM, also ceramic green bodies can be produced. Indeed thermoplastic polymers can be used as binder for ceramic powder and thermoplastic fused deposition AM technologies can be adapted and used also in the manufacturing of ceramics. These technologies have been recently successfully tested for the production of advanced ceramics as silicon nitride (Si3N4), aluminium oxide (Al2O3) and silicon carbide (SiC), however intense research is still needed in the raw materials development, conversion into a structural-stable ceramic and application-oriented optimization. Main challenges are suitable thermoplastic binder systems and their amount, shrinkage and cracks control during the high temperature treatment for the ceramic production, shape retention and final density of the final ceramic parts.

Despite their brittleness but thanks to their high stiffness, low coefficient of thermal expansion, high thermal conductivity and high thermal resistance, SiC-based ceramics are special candidates in aerospace and energy transformation field, for instance, as mirror structures for space optical devices and heat exchanger for high temperature and aggressive gases.

This work is a scientific experience starting from an innovative thermoplastic 3D printable binder system with crosslinking agent and ending in the production of complex-shaped dense SiC ceramic parts. The raw materials employed in the 3D printing process are cheap carbon and SiC powders compounded into pellets with the thermoplastic binder system. The pellets are practical feedstock for the 3D Printer that can produce layer by layer the green . After pyrolysis, the part is infiltrated with liquid silicon and converted to a dense SiC-based ceramic part. The use of Reactive Melt Infiltration instead of a traditional sintering process reduces the final treatment temperature significantly from far above 1600°C down to 1450°C.

Rheological and thermal properties of the feedstocks are measured. Scanning electron microscopy images are used to evaluate the microstructure and the final composition of the resulting ceramics. Coefficient of thermal expansion has been measured in different direction to assess the influence of the 3D printing process on the final ceramic properties. Moreover geometrical shape are checked along the processing chain and finally mechanical test are performed.

Keywords: Silicon Carbide ceramics, Thermoplastic binders, Reactive Melt Infiltration

ABS 396

FABRICATION AND MECHANICAL BEHAVIOUR OF CERAMIC/POLYMER POROUS SCAFFOLDS WITH CORE/SHELL ARCHITECTURE FOR BONE TISSUE REGENERATION

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Objective This study aims to develop novel ceramic/polymer composite scaffolds with a calcium phosphate shell and a biodegradable polymeric (polycaprolactone, PCL) core. This strategy preserves interconnected macro-porosity to promote cell ingrowth, vascularization, and diffusion of nutrients. Osteoconductivity is thus guaranteed while the ductile polymer enhances toughness.

Materials and Methods Ceramic water based inks for robocasting with high solid content were prepared to be extruded through a coaxial printing needle to obtain hollow rods scaffolds. Normal tips were used to obtain dense rods scaffolds for comparison.
Samples were sintered and then coaxial scaffolds with hollow rods were infiltrated with two different methods: injection of a PCL polymer solution into the rods at low temperature, and vacuum-assisted impregnation of the rods with PCL melt . For a complete characterization, three types of specimens have been fabricated and tested: hollow, hybrid and dense rods scaffolds.

Results Hollow structures show excellent shape retention, exhibiting channels accessible to the polymer for impregnation. Hybrid scaffolds were successfully obtained by impregnation with PCL from a polymer solution or a polymer melt, being the channels partially or completely occupied, respectively.
Under compression, although still weaker than dense scaffolds´ hybrid scaffolds are stronger than hollow samples, thanks to PCL sealing fracture precursor flaws . Toughness, estimated as strain energy density (SED), of hybrid scaffolds under compression is clearly superior to both all ceramic structures as the polymeric phase holds the structure after failure of the ceramic.
For bending loads, stress-stroke curves reveal typical brittle behavior in dense and hollow scaffolds, which contrasts with damage tolerance and retained mechanical integrity of the hybrid ones. While a alight loss of strength compared to dense rod scaffolds occurs, there is a dramatic increase of SED upon infiltration, especially in hybrid samples prepared by melt impregnation. Large stretched PCL filaments are evident, bridging the crack walls together after very large strains, long after the ceramic rods fail.

Conclusions It has been possible to fabricate hollow rods robocast scaffoldsand to infiltrate them with PCL. Melt impregnation is the optimal infiltration process for maximizing polymer penetration and the subsequent mechanical enhancement. Indeed, infiltration of PCL improves strength of hollow scaffoldsin compression and enhances toughness both in compression and, especially under bending stresses. The performance in terms of toughness is dramatic even over dense structures. Strength is lower than in dense-strut structures but in bending this difference is minor.

Keywords: coaxial, scaffold, bone

ABS 390

SYNTHESIS, CHARACTERIZATION AND DENSIFICATION OF Ag DOPED CERIA NANOPOWDERS

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Nanosized Ag-doped ceria (Ce1-xAgxO2-y) powders (0 - x - 0.04) were obtained by self-propagating room temperature reaction. X-ray diffraction analysis and field emission scanning microscopy results showed that the doped samples are solid solutions with fluorite-type structure and all powders were nanometric in size. The average size of Ce1-xAgxO2-y particles lies about 4 nm. Raman spectra revealed an increase in the amount of oxygen vacancies with the increase of Ag concentration. This increasing results in a narrowing of the bandgap of CeO2. The photocatalytic performances of the Ag-doped ceria solid solutions were evaluated by decomposing an organic dye, crystal violet under UV irradiation. The Ag-doped ceria solid solutions exhibit significantly better photocatalytic activity than the pure CeO2 and commercial TiO2. The densification process was studied by isothermal and microstructural development by scanning electron microscopy. By controlling the processing variables, it was possible to obtain high density samples with a homogeneous microstructure at low-temperature. A closer examination of silver doped ceria indicated that silver affects sintering by producing a liquid at the ceria grain boundaries. Due to this liquid phase sintering, it was possible to produce dense nanostructured ceria at lower temperatures.

Keywords: ceria, solid solution, oxygen vacancies

ABS 384

NOVEL STRATEGIES FOR BIOINSPIRED FREEZE-CAST GRAPHENE/CERAMIC COMPOSITES

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In the quest of finding novel materials that can endure the demands of the ever-growing engineering industry, graphene-based composites have emerged as one promising alternative in order to enhance the properties of current structural materials while providing additional functionalities. Despite its popularity, achieving an efficient graphene reinforcement in a matrix material remains a challenge as of today, which is especially critical amongst graphene/ceramic composites[1]. Such issue has facilitated the rise of graphene oxide as a key graphene precursor, due to its solubility in different solvents and its ability to restore the properties of graphene upon thermal or chemical reduction. Graphene/ceramic composites still show much room for improvement in terms of their fracture toughness and resistance to crack growth, for which it is believed that mimicking multi-hierarchical materials commonly found in nature, such as nacre or bone, could be crucial to increase the toughness and maintain high mechanical strength[2].

Our aim is to apply this strategy of bioinspiration by producing new graphene/ceramic composites combining freeze-casting (also known as ice-templating) and wet chemistry processing methods. The precursors selected are graphene oxide and alumina suspensions, both commercial and synthesised via sol-gel from aluminium lactate and chloride. Prior to infiltrating graphene scaffolds with the alumina slurries, we propose to integrate an intermediate step in order to tune the hydrophobicity of these graphene structures, formerly hydrophobic, and improve the chemical bonding with the ceramic slurry. The alignment of these graphene scaffolds has been confirmed by microscopy, while the interaction between both phases has been verified by various characterisation methods, such as Transmission Electron Microscopy (TEM) and Thermogravimetric Analysis (TGA). This work aims to showcase whether dense graphene/ceramic composites can be fabricated by embedding freeze-cast graphene structures in a ceramic matrix, leading to novel composite materials with optimised mechanical properties and added functionalities.

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Keywords: Graphene-based composites, Freeze-casting, Bioinspiration

ABS 382

MOLECULAR APPROACH TO NOVEL MULTIFUNCTIONAL HYBRID sp_2/sp_3 0D-NANOCARBON CONTAINING SILICON-BASED CERAMIC COMPOSITES

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The protection of the environment by increasing energy efficiency as well as by developing new clean energy sources is one of the most important global challenge our days. In order to fulfill all requirements for new technologies relevant to energy security, innovative “smart” composite materials with synergetic functions of their components are needed.

For the first time, polymer-to-ceramic conversion route was used for the in situ preparation of multifunctional 0D-carbon/ceramic nanocomposites (i.e., nanodiamond (ND)-ceramic and onion-like carbon (OLC)-ceramic nanocomposites). Chemically functionalized NDs can covalently bind at their surface with different organosilicon polymers and the resulting preceramic-polymer-based nanocomposites can be used as tailored precursors for the production of novel nanoscaled nanocarbon-ceramic composites which can display excellent mechanical properties as well as interesting functional properties. Their properties are related to the chemism of the precursors as well as to the thermal treatment conditions. Thus, a careful design of different ceramic microstructures was obtained by changing the chemistry of the precursors, concentration of the 0D-nanocarbon phase, processing route, atmosphere of thermal annealing as well as the temperature of pyrolysis (from 700 to 2000 °C).

Novel SiO2- and Si3N4-0D-nanocarbon ceramic composites were produced upon the pyrolysis of preceramic precursors consisting of a highly crosslinked polysiloxanes and polysilazanes covalently functionalized with nanodiamonds. As the polymers deliver C-free SiO2 and Si3N4 upon pyrolysis, the nanocarbons were the exclusive carbon source in the obtained ceramics. Using intermediary temperatures of pyrolysis in inert atmosphere or vacuum, novel nanocomposites containing a hybrid core-shell sp2/sp3 0D-nanocarbon phase, named bucky nanodiamond phase, can be produced. The bucky nanodiamond phase combines the properties of nanodiamonds and those of fullerenes in one material and therefore, it confers exceptional multifunctional properties to their nanocomposites.

The nanocomposites were structurally characterized and their thermal stability against crystallization and decomposition will be presented. Furthermore, selected functional properties thereof will be highlighted and discussed within the context of prospective energy-related applications.

Keywords: nanocarbon, silicon-based nanocomposites, multifunctional materials

ABS 378

CONTROLLING OF FABRICATION ACCURACY AND PERFORMANCE OF CERAMIC MOLDS WITH INTEGRAL CORE/SHELL FOR ADVANCED TURBINE BLADES

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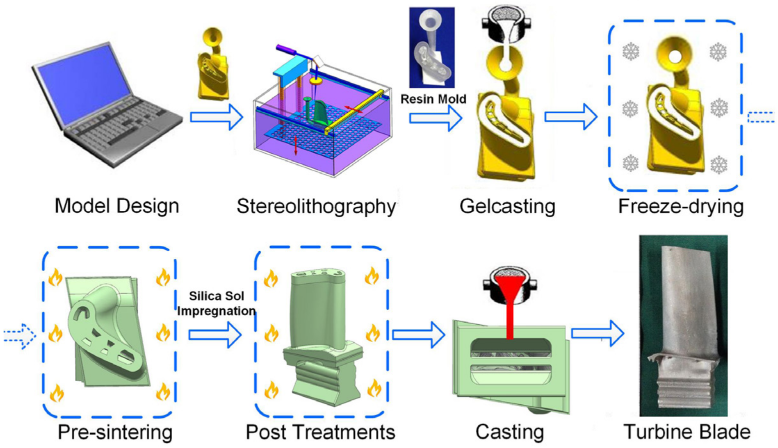
Turbine blades are the key components of the hot sections in aero-engines and gas turbines. Due to the restrictions of mold design and manufacturing technology, the investment casting process cannot meet the manufacturing requirements of advanced turbine blades with high efficiency and precision. Based on the additive manufacturing technique and gelcasting process, we proposed a rapid manufacturing process of ceramic molds with integral core/shell structures. Combined with the precision casting technology, this process has been expected to realize the manufacturing of advanced turbine blades rapidly.

The duplication of tiny structures inside the ceramic molds were realized by gelcasting. The closest packing formula for the multi-level gradations by using irregular particles was deduced. And the ratios between coarse and fine particles under different gradation numbers were determined. A ceramic slurry with a low viscosity and high solid loading were prepared by a tetramodal system. The maximum solid loading was 62vol%, and the viscosity was only 0.29Pa.s. The vacuum injection technology was also adopted to improve the duplication ability of slurry towards tiny structures. The control methods of structural integrity and position accuracy of ceramic cores during pre-sintering were put forward. The mechanical properties in pre-sintering were improved after adding polydimethylsiloxane (PDMS), which had a low pyrolysis rate during heating. The bending strength at 500°C of cermamic molds with PDMS was greatly improved form 0 to 1.037MPa, when 4wt% PDMS was added. The structural integrity was maintained after pre-sintering. A method of suppressing the creep deformation of specific cores by adjusting the placement of mold in the sintering furnace was proposed, which was called the Barycenter-Plane Method. By using this method, and the maximum shift at the bottom of U-bend cores was reduced from 1.5mm to less than 0.1mm. The position accuray of cores was guaranteed. The high-temperature strengths of ceramic molds were increased, and the sintering shinkages were controlled. The formation mechanisms of high-temperature enhanced phases were investigated. The high-temperature strengths could be adjusted between 18.5 and 34.9MPa at 1500°C. Based on the principle of reactive sintering, zirconium aluminum alloy and aluminum silicon alloy were chosen as the pre-sintering and final sintering expansion agents, respectively. The sintering shrinkages were controled during the whole process. After optimization, the pre-sintering shrinkage was only -0.035%, and the final sintering shrinkage was only -0.045%.Finally, fabrications of advanced blades of aero-engines and gas turbines were realized by the aboved mentioned ceramic molds.

Keywords: Gelcasting, Ceramic mold for casting blade, Integral core shell structure



ABS 376

SELECTIVE CONTROL OF CRYSTAL STRUCTURES IN POTASSIUM SODIUM NIOBATE PARTICLES THROUGH A FACILE SOLUTION CHEMICAL SYNTHESIS

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Control over the precise crystal structure of functional materials has been desired to tune their physicochemical properties for their target applications. In the case of perovskite ferroelectric materials, the magnitude and direction of electric polarization are quite different depending on the crystal symmetries, leading to completely different properties such as ferroelectricity, piezoelectricity, and nonlinear optical properties. Although crystal structure of given materials adopts the most thermodynamically stable phase at given temperature and pressure, metastable phase could be kinetically evolved under a specific reaction condition in wet chemical synthesis. Here, we propose the strategy for controlling structures of K1-xNaxNbO3 particles with three different phases (orthorhombic, monoclinic, cubic symmetry) through a solution chemical synthesis. We also show a flexible hybrid composite generator enabled by K1-xNaxNbO3 particles-embedded polymer matrix.

Keywords: crystal structure, solution synthesis, potassium sodium niobate

ABS 375

MESOPOROUS FIBROUS SILICON NITRIDE BY CATALYTIC NITRIDATION OF SILICON AND SELECTIVE LASER MELTING

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The overwhelming majority of the mesoporous materials are represented by oxide ceramics; however, they do not compare favorably to silicon nitride in terms of breaking strength, dimensional stability, and high temperature and corrosion resistance. Mesoporous Si3N4 ceramics with tailorable internal structure, light weight, superb thermal shock resistance, high strain and damage tolerance, are promising candidates to be exploited as catalyst supports, bioreactors and high temperature gas filtering materials. In this work mesoporous fibrous networks were generated by two different methods: 1) Wet-combustion of transition metal oxide nano-catalysts using alumina nano-whisker (AW) support and catalytic nitridation of silicon; 2) Selective laser melting of catalysed Si, followed by further nitridation.

The catalytic effect of metal oxide and alumina whiskers was evaluated on their ability to drive the nitridation process of silicon in order to generate the mesoporous fibrous silicon network. Porous silicon nitride networks with a porosity of 45-52%, pore sizes in the range of 370-1200 nm, and median pore in the range of 495-1655 nm were produced. Networks contain silicon nitride fibres with a diameter of 400-500 nm and a length of up to few micrometres.

Parametric study of the selective laser melting process was performed to optimize the laser printing parameters: laser current, point distance, and exposure time. Silicon shapes with different porosity were produced. The nitridation efficiency achieved 50% with Ni-based catalyst subjecting growth of Si3N4 nanofibers on the surface and pores of the component.

Keywords: Silicon Nitride, Mesoporous structures, Selective laser melting

ABS 356

TRIDIMENSIONAL PRINTING OF STRUCTURES FROM COLLOIDAL INKS BASED ON GRAPHENE OXIDE USED AS PLATFORM FOR HYBRID MATERIALS

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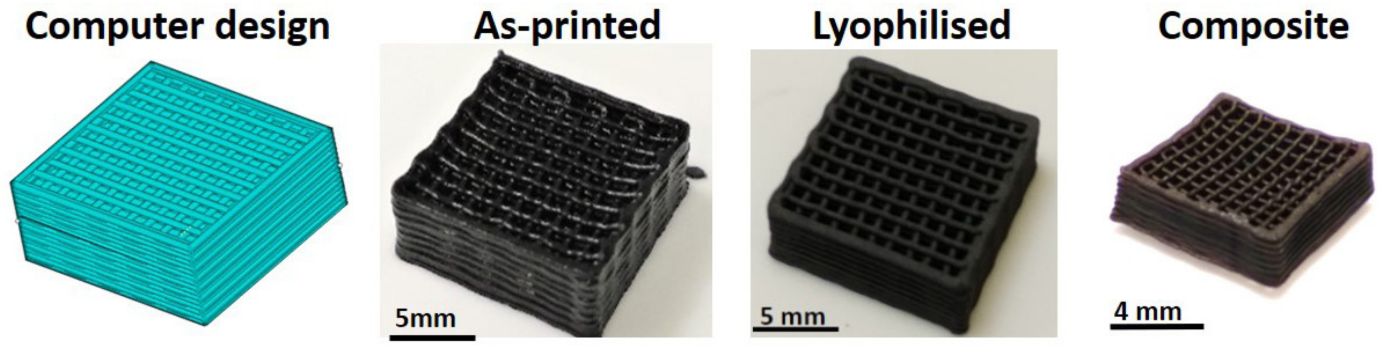
Direct ink printing has been used for developing complex computer-designed ceramic architectures by controlled filament deposition in layer by layer fashion. We propose using this technique for printing 3D stable scaffolds of 2D materials like graphene oxide nano-sheets (GO) and producing a hybrid material by a preceramic route while maintaining the aspect of the printed GO structure. The liquid preceramic polymer quickly infiltrates the 3D scaffolds under vacuum conditions leaving practically no porosity in the filaments as tomographic images showed. The water-based inks with about 5 wt. % GO present a shear thinning rheology provided by the addition of different polyelectrolytes. The water content in the GO scaffolds is removed by following two different routes: ambient exposure and lyophilization the structures after freezing. This last freezing step is critical in order to achieve crack-free smooth surface scaffolds. These graphene oxide/ceramic composite structures are electrically conductive (σ =1 700 S/m at RT) and, in addition, the ceramic hybridization allows increasing the mechanical compressive strength about 700% with respect to the single GO structure, as well as their thermal stability up to 1000ºC, thus obtaining structures highly conductive and stable at relatively high temperatures. The hybrid structures can be of interest for thermal dissipation, energy storage or catalytic processes.

Keywords: 3D printing, Graphene, Composite



ABS 350

HYDROTHERMALLY DERIVED DOPED CERIA NANOCATALYST

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Cerium dioxide or ceria (CeO2) is a rare earth metal oxide of great importance with numerous applications in industry, energetics and environmental protection. Catalytic oxidation of volatile organic compounds (VOCs) has been a burning issue over the last couple of years and ceria has been considered a useful catalyst for this process, especially in the nanosized form due to the increased specific surface area. The advantages of ceria are reversible oxygen storage and release capacity, resistance to poisoning and low cost, but the possible problems are poor low-temperature catalytic activity and thermal stability. For this reason, various transition metals, such as Mn, Fe, Co, etc., are doped into the ceria crystal lattice to improve its properties. In this work, pure and doped ceria nanocatalysts have been obtained through a simple, affordable and environmentally friendly method - the hydrothermal synthesis, which involves metal salts in sodium hydroxide solution under high pressure and temperature. In the doped samples, 10 mol % of cerium was replaced with Mn, Fe, Co, Ni, Cu and Zn ions. The prepared samples were characterized in detail using X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDX), Fourier-transformed infrared spectroscopy (FTIR) and adsorption-desorption N2 isotherms, while the catalytic activity tests were based on toluene oxidation process in a tube reactor with a fixed layer of catalyst.

The XRD results showed only ceria in samples doped with Cu, Mn, and Zn, while other doped samples displayed the presence of additional crystallographic phases. The application of the Scherrer method revealed that the ceria crystallite sizes were between 3 and 5 nm. Approximately the same particle size could be estimated based on the TEM micrographs. Small particle sizes resulted in a high specific surface area of the prepared nanocatalysts. Ceria doped with Cu and Mn revealed substantial catalytic activity, samples with Fe, Ni and Zn showed no significant improvement of catalytic activity, while ceria doped with Co exhibited a decrease in catalytic activity for the toluene oxidation process.

The obtained results are more than satisfactory and encourage us to deepen our investigation of the doped ceria nanocatalyst, specifically the Cu- and Mn-doped one, and its potential catalytic applications.

Keywords: hydrothermal synthesis, doped ceria, nanocatalyst

ABS 348

NANO SIZED 3D PRINTING AND MOTION CONTROL BY NANO SECOND PULSED FIELD

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This study aims to elucidate the mechanism of driving nano/micro dielectric ceramics particles under the nano second pulse or DC electric field. The microstructure driving is affected by various electrical phenomena occurring at the same time such as surface potential, polarization, and electrostatic force. It makes the challenge to clarify the driving mechanism. A simple experimental system was used to observe the behavior of the ceramics nano particles and spherical micro ZrO2 particles in a nonaqueous solution under the electric field. The results suggested that the driving mechanism of the ceramics nano particles and ZrO2 particles under electric field was created by the combination of the electric image force, the gradient force, and the contact charging phenomenon. It is propose a method to control the micro/nano structure by using this motion control mechanism in the further studying and application.

Keywords: Electric Field, Particle Control, Nano Second pulsed power

ABS 340

IMPROVING HYDROXYAPATITE BIO-CERAMIC POWDER ABSORPTANCE AT Nd-YAG LASER WAVELENGTH BY ADDITION OF ABSORBING ADDITIVES

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Additive manufacturing technologies allow the shaping of bioceramic parts with complex structures and ideal properties, as tissue repair material, like bioactivity and biocompatibility to ensure a good osseointegration/ osseoincorporation of the implants as well as good mechanical and chemical resistance [1]. The selective laser melting/sintering of a powder bed (SLS/M) as additive manufacturing (AM) technique allows convenient, fast, and individualized implants and shorten the production period of patient matched tissue engineering scaffolds from a powder feedstock, as Hydroxyapatite (HAP) powder. However, a deeper study of the optical properties of the bioceramic raw materials is crucial when using the SLS/M technique. Ceramic powders absorptance at Nd-YAG laser wavelength (1.06µm) is not enough to produce a suitable heat/ matter exchange between the particles to trigger the material densification. Improving the laser radiation absorption by mean of use of absorbing additives is of particular interest because it allows to control the porosity, interconnected pores and to avoid the formation of cracks during SLS/M technique [2].

In this communication, we discuss the influence of a commercial graphite (TIMREX KS44) as absorbing additive in the absorptance of HAP powder at Nd-YAG laser wavelength. The absorptance is measured on different single and two components powders to elucidate the relevant proportion for a correct shaping and yield while maintaining appropriate product properties.

Different mixtures were prepared with a mass of graphite in the range of 0% and 2.5% by mechanical mixing. Taking into account that the absorptance of pure ceramic powders at the same wavelength is lower than 5% the measurements indicate that, with small proportions of absorbing additive in the mixture, the cabsorptance of the composite powder increases significantly. For example, a value of absorptance higher than 40% was observed from the mixture containing a proportion of 0.75% of graphite mass onwards. This value is close to the one observed in metal powders often used in SLS/M and it is expected to be higher enough for the use of the ceramic composite powder in AM technologies. Some simple bioceramic parts using this composite powder were shaped in additive manufacturing machine equipped with a laser Nd :YAG showing promising results.

Acknowledgements
This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 764935

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Keywords: 3D printing, Hydroxyapatite, Bone tissue engineering

ABS 659

HYBRID MACHINING FOR RAPID PROTOTYPING OF CERAMICS

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Fabricating ceramic parts with a high degree of complexity and fine details remains highly challenging. Additive manufacturing (especially stereolithography) is promising but it is still far from maturity. It suffers from a lack of reliability and cannot provide defect free parts except for very specific geometries.

Hybrid manufacturing is a term that typically describes integration of multiple unit manufacturing processes into one machine. The combination of several technologies in one single device is meant to enable shorter processing time, reduced inspection time and handling while decreasing the cut production costs of products. It also aims at producing parts exhibiting a greater design freedom or intricacy and sometimes radical geometries that conventional manufacturing is not able to produce.

In this presentation, an original hybrid manufacturing approach conceived for ceramics is presented. It combines in a single setup conventional CNC machining of ceramics in the green state with laser milling. This combination allows a dramatic reduction of the manufacturing time (at least by an order of magnitude) especially for parts exhibiting very fine and delicate features (< 0.2 mm).

The European Regional Development Fund (ERDF) and Wallonia, are gratefully acknowledged for their financial support to these research projects: CERAMPLUS and HYBRILUX.

Keywords: Machining, Laser, Green ceramics

ABS 332

SOFT CHEMISTRY MICROWAVE ASSISTED NANO-STRUCTURED COATINGS ELABORATION FOR SELF-CLEANING AND ANTIBACTERIAL USES

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Objectives Hygiene of equipment in contact of users is an important issue in railroad industry. The numerous cleanings in order to eliminate bacteria and dirt cost a lot. Besides, mechanical solicitations on contact parts are observed daily. It should be interesting to consider a better adhesion, wear resisting solution that can also bring a self-cleaning and antibacterial aspect. Thus, a Hauts-de-France and Maubeuge Val-de-Sambre conurbation authority co-financed PhD thesis has been set up since October 2017 based on anterior studies carried by the Laboratory of Ceramic Materials and Processing.

Material and methods To accomplish this task, an aqueous chemical method has been implemented. This protocol should be assisted by microwave to minimize environmental impact. It involves nanometric liquid zinc oxide synthesis under 100°C. The originality here consists in a variation of surface texturation by modification of the synthesis time or concentration of the species in solution. This should help to adjust wettability (lotus leaf effect). Nanostructured zinc oxide has been chosen because of the inherent photocatalytic effect, which can activate organic substance degradation.
Tested subtracts are made of stainless steel to conform to transport uses. Substract preparation and adherence of the coating was the first aspect of this study. A large scale of roughness were prepared and a meticulous cleaning of the samples is applied.
The main goal of the elaboration protocol is to fix enough Zinc based seeds to make them grow during the next step as desired (nanorods). To improve this adhesion, a Silica gel has been formulated and optimized to be applied as a chemical base.
A last step consisting of adding by vapor deposition a wide carbonated organosilane compound allows enhancing the superhydrophobic power of the coating.

Results A study about process optimization especially on the seed synthesis will be shown and the quasi-proportionality between the reaction time and the nanorod length will be demonstrated. In addition, Water Contact (superior to 150°) and Roll-off Angle at different steps of the process will be presented. First results of photodegradation are presented.

Conclusion A green, easy-to-process and control coating with self-cleaning and antibacterial properties has been synthetized with a satisfying surface structuration.

Keywords: sol-gel, photocatalysis, coating

ABS 331

PHASE FORMATION AND DISPERSITY OF 8Y_2O_3-92ZrO_2 PRECURSORS (MOL.%), OBTAINED BY HYDROTHERMAL TREATMENT

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In the recent years, there is a strong call for high volume (low cost) of nanosized oxide powders development. Hydrothermal technique is considered one of the most promising for the targeted crystallization of solid solutions (as well as zirconia based solid solutions) at rather low temperatures. A number of variations of the hydrothermal technique is known so far as, e.g., direct hydrothermal crystallization, hydrothermal precipitation, hydrothermal oxidation, etc. Hydrothermal synthesis has several advantages over the other techniques for oxides synthesis, such as precise stoichiometry control of the resulting solid solutions, as well as the particle size distribution of the resulting oxides, their morphology and crystal structure. Thus, the goal of the work was to study the effect of hydrothermal treatment conditions on the crystallization processes and powders structure in 8Y2O3-92ZrO2 (mol.%) precursor. The processes were investigated in the critical and subcritical conditions.

Gels of stabilized zirconia were obtained by sol-gel synthesis method in the reverse co-precipitation variance. Mixed solution of the initial salts ZrO(NO3)2·5,5H2O, Y(NO3)3·6H2O of various concentration was used. The precipitant was 1 M aqueous ammonia solution and synthesis conditions were T = 1-2°C, pH = 9-10. Then, the initial solutions, and freshly prepared gel, and freeze-dried amorphous powders were subjected to hydrothermal synthesis at different temperatures and, further, dried to constant weight at 110 ° C. In order to establish the phase composition, samples morphology, and crystallization temperature of the solid solution, precursors obtained were comprehensively investigated by the following methods: simultaneous thermal analysis, X-ray diffraction analysis, scanning electron microscopy, particle size distribution analysis. The pressure in the system during the hydrothermal experiment was calculated and compared with the literature data on the water critical pressure.

Via XRD analysis it was established that the beginning of crystallization is observed after hydrothermal treatment of precursor at 200 °C in the critical conditions. Hydrothermal treatment in critical conditions at the higher temperatures (up to 320 °C) results in low-crystalline cubic zirconia based solid solution. Precursors obtained in subcritical conditions up to 280 °C remain amorphous. Deagglomeration of powders is observed up on the increase of treatment temperature in subcritical conditions. The average agglomerate size in powders lies in the range of 0.97-1.36 μm. The hydrothermal treatment of the decimolar solution results in the direct crystallization of needled shaped crystals of the baddeleite phase. DSC and TG studies were performed at the Center for X-ray Diffraction of St Petersburg State University. SEM studies were performed at the center for nanotechnologies at the research park of St Petersburg State University.

Keywords: Zirconia, Hydrothermal treatment

ABS 328

ELABORATION OF LEAD-FREE PIEZOELECTRIC MATERIALS FOR THICK FILMS COATING BY AEROSOL DEPOSITION

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CTTC and IRCER have developed an innovative and novel 3D printing method of thick films coatings. This process called INPACT is based on the Aerosol Deposition Method (ADM or AD), also called Vacuum Kinetic Spray (VKS) and has led to the development of a Computer-Aided Manufacturing (CAM) machine [1], in order to get complex 2D-3D-shapes.
The principle of ADM [2] is to project a gaseous aerosol of dry particles onto a substrate (which doesn't require any surface preparation) through a supersonic nozzle. The kinetic energy of particles implies fragmentation and a cohesion phenomenon coupled with local thermal losses. Although the consolidation mechanisms are not fully understood yet, ADM is a low-cost method for the fabrication of dense films without post-coating thermal treatment. A huge innovation could be the manufacturing of dense ceramics on new and multiple kinds of substrates including metals or even low melting temperature or flexible materials like plastics or polymers for electronic and microelectronic applications for instance.

This talk is focused on the deposition of lead-free piezoelectric ceramics with perovskite structure for energy harvesting applications. Indeed, we have worked to realize our own synthesis protocol of ceramics powders, suitable for ADM process. The powder, the piezoelectric thick coating elaboration and characterisation will be presented to show all potentials of this technique.

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Keywords: aerosol deposition, thick films, lead-free piezoelectric

ABS 316

PLASMA SPRAYED BIOACTIVE GLASS COATINGS DEPOSITED WITH TWO DIFFERENT PLASMA TORCHES

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Bioactive glass coatings are emerging as substitutes of hydroxyapatite ones due to their higher ability to react in biological environments. Among other methods such as enamelling, magnetron sputtering or pulsed laser deposition, plasma spraying is the one of the most studied and used technique for the deposition of this type of coatings. Moreover, during last decades, plasma torches have been evolving to reach more and more powerful plasma jets. Therefore, the present work aims to deposit plasma sprayed bioactive glass coatings by using two plasma torches.

A commercial bioactive glass powder with the same composition of the 45S5 bioglass was used as feedstock. A mono-cathode torch (F4-MB, Oerlikon Metco) and a tri-cathode torch (Triplex Pro, Oerlikon Metco) were employed to deposit the bioactive coatings. The first torch works with argon as primary gas and hydrogen as secondary gas, while in the second one argon was kept as primary gas and helium was used as secondary gas. In both torches, the flow rate of the gases as well as the input current were varied to find optimum spraying parameters. All coatings were microstructurally characterised by scanning electron microscopy, X-ray dispersive energy analysis and X-ray diffraction. Thickness and porosity were also determined. In addition, the bioreactivity of the sprayed coatings was determined by immersing them in Simulated Fluid (SBF) until 14 days.

For the spraying parameters used, all coatings displayed an amorphous character. However, with the utilisation of the Triplex Pro torch it was possible to develop coatings with the same thickness as those deposited with the F4 torch, with lower porosity and higher microstructure homogeneity. On the other hand, X-ray dispersive energy analysis revealed lower amounts of sodium and phosphorous at the surrounding of the splats in all coatings, due to the volatilisation of these elements in the plasma jet. Concerning the bioreactivity of the coatings, all of them have reacted with the SBF and displayed an hydroxycarbonate apatite layer on their surface.

Triplex Pro could be a suitable plasma torch to deposit bioactive glass coatings, since the microstructures developed are much better than those sprayed with F4. However, more research should be carried out in order to optimise the spraying parameters with the aim of preserving the resulting microstructure and reducing the volatilization of sodium and phosphorus.

This work has been supported by Research Promotion Plan of the Universitat Jaume I through action 2 (E-2018-20) and action 3.1. (PREDOC/2015/50).

Keywords: 45S5 bioactive glass, Atmospheric plasma spraying, Bioactive coatings

ABS 314

SHRINKAGE BEHAVIOUR OF CERAMIC BODIES DURING DRYING: FOLLOWING EXTRUSION OR PRESSING

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Most fabrication processes for ceramic products, traditional and technical, involve forming the basic shape of the ceramic with a solid/liquid paste or suspension. Consequently, a drying step is necessary before firing the products at high temperature. This step can be critical, mainly due to the shrinkage that can cause damage in the final product, both for forming methods recently developed (tape casting) or traditional methods (slip casting, jiggering, pressing). Understanding the drying behaviour is then a necessity to optimize this step and obtain high quality samples for industrial applications. This study focuses on green bodies shaped by extrusion and by pressing of ceramic pastes.

One of the widely used methods to examine the behaviour of a ceramic consists of monitoring the length and mass during drying. A new optical method has been developed in order to follow dimensional changes, in two directions, simultaneously with the mass. The results are analyzed through the Bigot curve (water content as a function of shrinkage). Two different ceramic materials were studied: alumina and kaolin. Alumina was chosen for its frequent use in technical ceramics, while kaolin is mainly used for the manufacture of traditional ceramics. Another point is that these two materials have different grain morphologies: equiaxed for alumina and tabular for kaolin.

For each material, Bigot curves reveal two distinct regimes. The first one corresponds to a linear decrease of dimensions with water loss. Then in the second regime, shrinkage becomes negligible for the remaining drying time. For alumina samples shaped by pressing, the overall shrinkage does not vary with direction. In other words, an isotropic behaviour is noted. However, for kaolin samples, overall shrinkage values are different in different orthogonal directions, revealing an anisotropic behaviour. For instance, for extruded samples, the shrinkage value corresponding to the perpendicular extrusion axis is 5% higher than in the other directions. This aspect can be related to the platelet morphology of the grains, which are oriented parallel to the extrusion axis. This specific orientation then influences the water location between grains yielding anisotropy. Similarly, for pressed samples, an anisotropy is observed with the strongest shrinkage along the direction corresponding to the pressing axis.

Finally, these results bring useful information on the shrinkage behaviour of ceramic green bodies, which is a critical step in the processing technology during drying. Controlling shrinkage is required to obtain high quality products.

Keywords: Drying,2D shrinkage, Extrusion

ABS 303

IMPROVEMENT OF FRACTURE STRENGTH IN CERAMIC MOLD AND CORE THROUGH APPLICATION OF INORGANIC BINDER

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Objective An organic binder called resin is employed to prepare the mold and core used in a conventional casting [1]. Therefore, the green strength of the mold and core is caused by chain entanglement of the polymer. However, the organic binder has a high possibility that the molded is broken during the casting due to the loosening of the chains and the cohesion between the chains. In order to overcome this disadvantage, a molded was manufactured using sodium silicate such as water glass, instead of organic binder [2]. The green was strengthened by a post-process with an inorganic binder.
Materials & Method A green formed with a mixture of mullite (3Al2O3·2SiO2) bead and water glass was dipped in an inorganic binder precursor composed of silicate and sodium metoxide. Through the condensation reaction between water glass and methyl alcohol contained in the inorganic binder, the green strength was improvement. After the dipping, the dried sample was heat treated at 1000 °C for the glassification of sodium silicate.
Results Figure 1 shows the green and firing strengths of the samples prepared with water glass solution before and after heat-treatment. The overall fracture strengths of the samples with the water glass (Runs B/C/D) were increased compared with that of the sample with the organic binder (Run A). The green and firing strengths were enhanced by hardening between water glass molecules and with increasing the amount of the glass phase produced from the water glass and inorganic binder, respectively. The highest fracture strength was obtained when the 20 vol% water glass was employed as the forming binder (Run C). However, when the water glass was more added over 20 vol%, the strength adversely affected (Run D). When a large amount of water glass was employed to prepare a green , the starting particles become fluid and cause internal defects. Microstructure of sample prepared using the water glass showed a thicker reaction layer and produced more glass phase (Run C, in Fig. 2). The sample was completely decomposed in NaOH solution at a relatively low temperature of 60 °C (Fig. 3)
Conclusions In preparation of ceramic mold and core, the glass water solution improved fracture strength by combining the inorganic binder in a post-process. In the 20 vol% water glass, the sample showed and reasonable strength and 100% elution

Keywords: Water glass, Inorganic binder, Post-process

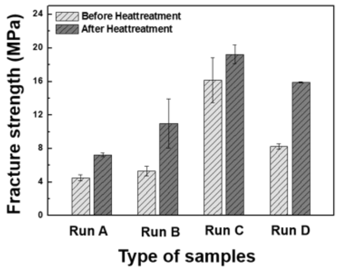

Fig. 1. Fracture strength of samples with the type and content of forming binder. Runs A, B, C, and D indicate fracture strengths of samples prepared with 5 vol% organic binder, 5 vol% water glass, 20 vol% water glass, and 25 vol% water glass (Run D), respectively.

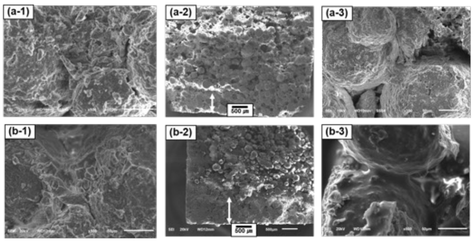

Fig. 2. Microstructure of samples with forming binder: (a) sample prepared with organic binder (Run A) and (b) sample prepared with 20 vol% water glass (Run C). Each number indicates green microstructure, low magnification after 1000°C, and high magnification after 1000°C, respectively.

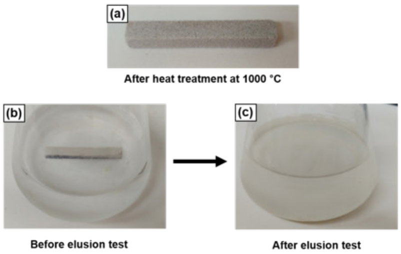

Fig. 3. Elusion result for sample prepared with Run C in Fig. 1: (a) as-prepared sample at 1000 °C, (b) before elusion test, and (c) after 24 h in NaOH solution.

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LITHOGRAPHY-BASED CERAMIC MANUFACTURING OF JOINT REPLACEMENTS: MICROSTRUCTURE AND SURFACE FINISHING ANALYSIS

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The lithography-based additive manufacturing (L-AM) is more and more experimented for ceramics and biomaterials. The advantages of this process include a high accuracy (up to 30 μm), good mechanical properties and surface finishing. The study focused on the production of orthopaedic ceramic prostheses for small joints or extremities through Digital Light Processing (DLP), a L-AM technique which consists of selectively curing a resin with a LED light source to build up the part. Each layer is defined by a digital micromirror device that allows to turn on and off its pixels creating the section contour. Various materials were tested: alumina, zirconia and hydroxyapatite. After the conventional post-treatments to burnout the blinder and sinter the green parts, FTIR spectroscopy and X-ray diffraction analyses were carried out to verify their crystalline phase and chemical composition. Finally, the surface quality of printed components was studied through SEM microanalysis and profilometry, to compare the superficial finishing level of the different materials.

Keywords: Stereolithography, Orthopedic prosthesis

ABS 294

ADDITIVE MANUFACTURING OF CERAMICS BY MICRO EXTRUSION OF COMPOSITE GRANULATES

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Objective Nowadays Filament printing is an established standard technology for additive manufacturing of polymers. For ceramics, feasibility of production of highly powder filled filaments and printing of those is demonstrated, but several drawbacks and issues like filament buckling, rapture or nozzle clogging must be taken into account. The requirements of filament properties and production process lead to a reduced degree of freedom.

An alternative process is presented, where instead of prefabricated filaments powder/polymer composites are fed as granulates into a single screw micro extruder. The extruder is integrated into a 3D printer architecture. Characterization of geometrical specifications as well as strength and density data demonstrate the current status and potential of the developed technique for additive manufacturing of ceramics.

Materials & Methods A micro extrusion printer was developed and used to print demo objects and test specimen to investigate printing and material specifications. As main standard material Al2O3 was chosen, which was compounded with thermoplastic ethylene vinyl acetate copolymer (EVA) and process additives. Printed parts were debinded in a two steps process and subsequently fired to nearly full density. In addition to Al2O3 other ceramic materials where formulated as well in a similar manner.

Series of bars were printed and converted to ceramics to characterize four-point bending strength distribution and Weibull modulus depending on print and infill directions and pattern as well as post print surface finish. Microstructure, mechanical strength and density values were compared to uniaxial pressed bars of the same powder under identical firing conditions.

Results The developed micro extruder is able to print high quality ceramic parts out of thermoplastic polymer / ceramic powder composite granulates. Objects could be printed to nearly full density. Strength is partially anisotropic, depending on the direction of printing pattern. Surface finish procedures prior to or after firing increases the level of strength due to removal of defects and roughness. The level of strength and density is close to standard alumina ceramics.

Conclusions Additive manufacturing of ceramics by micro extrusion of composite granulates is a straightforward method of filament printing, circumventing issues of production and properties of feed filaments. A higher level of flexibility of formulations is beneficial for adjusting melt rheology, print parameters, debinding conditions and hence final material properties. This is demonstrated by the production and characterization of high quality alumina and other ceramics.

Keywords: Filament printing, Micro extrusion, Mechanical Characterization

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FDM-3D PRINTING OF SOFCs

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The recent development of additive manufacturing (AM) technologies applied to three-dimensional printing (3D-printing) of electrochemical energy devices offers the possibility to develop cost effective, free shape and optimized performance systems. In this technological sphere, the search for novel available materials and/or 3D-printing processes constitutes one of the main goals; achieving this will necessarily lead to overcoming the manufacturing limitations of ceramics materials for Energy applications. [1-3]
We have developed a proprietary procedure [4] to print a solid oxide fuel cell (SOFC) from the ceramic materials processed as a filament to the final free-form cell using fused deposition modelling. The most significant characteristic of this method is its flexibility that allows the use of several ceramics without significant changes. Currently, cells obtained using this technology exhibit electrochemical performances comparable to traditional fabrication methods (Fig. 1a). The main drawbacks relate to the inherent characteristics of additive technology, i.e. the fabrication by addition of layer-upon-layer of material (Fig. 1b and 1c). This provides additional physical barriers that results in lower overall electrical conductivity; strategies pursuing to minimise these fabrication characteristics (i.e. overlapping optimization, sintering aids …) are currently in progress.
The filament formulation offers the possibility of including pore formers to precisely control the porosity in the resulting sintered ceramics and therefore facilitate the gas access to electrochemically active sites of SOFC electrodes and the evacuation of exhaust products (Fig. 1d and 1e).

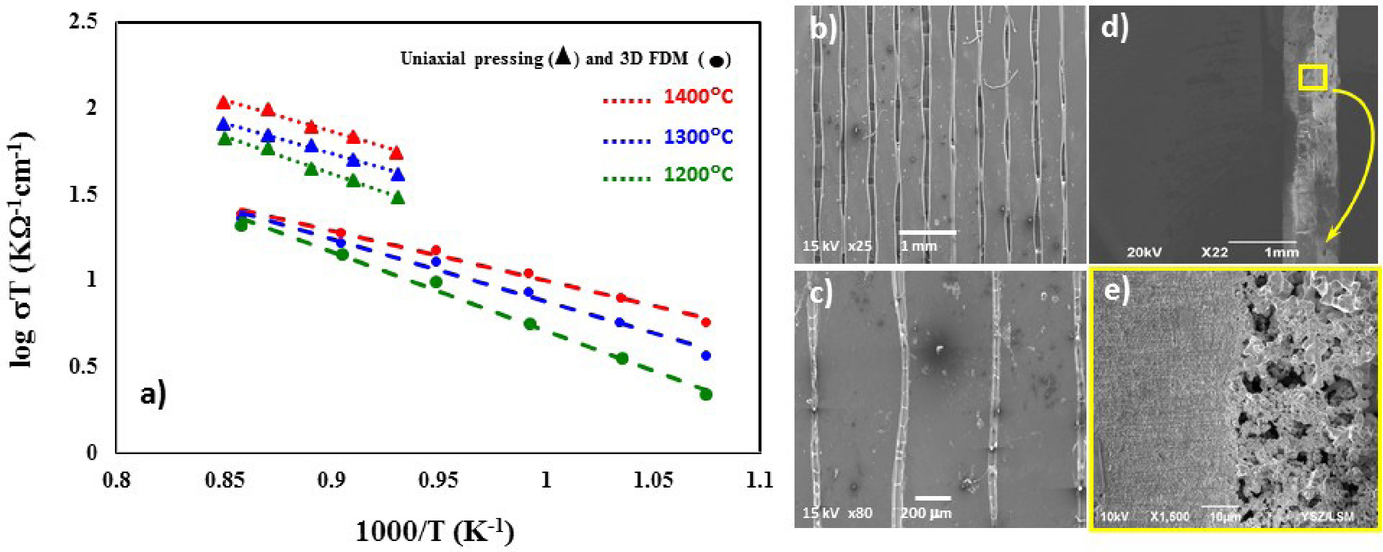

Fig. 1: a) Arrhenius plot (conductivity vs. temperature) for printed FDM and conventional uniaxially pressed YSZ after sintering in the 1200-1400 C temperature range; b) and c) SEM images showing the AM pattern; d) and e) Electrolyte-electrode interface of 3D printed SOFCs

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Keywords: FDM,SOFC, characterisation

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POTENTIAL OF AEROSOL JET PRINTING FOR MICROFABRICATION OF ELECTRONIC COMPONENTS COMPRISING CERAMICS

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Telecommunication and electronic industries are of great interest in novel direct-writing digital printing techniques. One of the emerging non-contact technologies is the Aerosol Jet printing technique. Main advantages of this technique are the flexibility of design and the possibility of more precise and non-contact deposition. The aerodynamic focusing of an aerosol stream also allows printing onto nonplanar, inclined or curved substrates.

The Aerosol Jet is mainly used for deposition of electric 2D conductive structures and can be also applied for other inks containing functional materials like plastics or ceramic materials (dielectrics, magnetics, insulators, piezoelectrics…). This presentation aims to show the potential of this technology through examples of ceramic layers and related properties.

The Aerosol Jet technology in comparison with Ink Jet technology permits utilization of wide range of inks viscosity. However, the most of commercialized inks dedicated for the Aerosol Jet printing are composed of metallic conductors (Ag, Au, Pt…). For this reason, CTTC works on development of compatible inks charged with ceramic particles of different nature. These new formulations are optimized and tested with various operational conditions in order to obtain high resolution printing features and desired functionality. The printed ceramic layers are then subjected to heat treatment and results showing the typical accuracy and their microstructure are presented.

The final goal of this work is to demonstrate that Aerosol Jet can be an accurate solution for elaboration of fully printed multilayered micro- components comprising ceramics, such like MLCC (Multi Layer Ceramic Capacitor), LTCC/HTTC (Low /High Temperature Cofired Ceramics) and others.

Keywords: Aerosol Jet Printing, multilayer, multimaterial

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COMPARISON OF MICROWAVE AND CONVENTIONAL SINTERING ON THE PROPERTIES AND MICROSTRUCTURE OF STEREOLITHOGRAPHY CERAMIC MANUFACTURED PARTS

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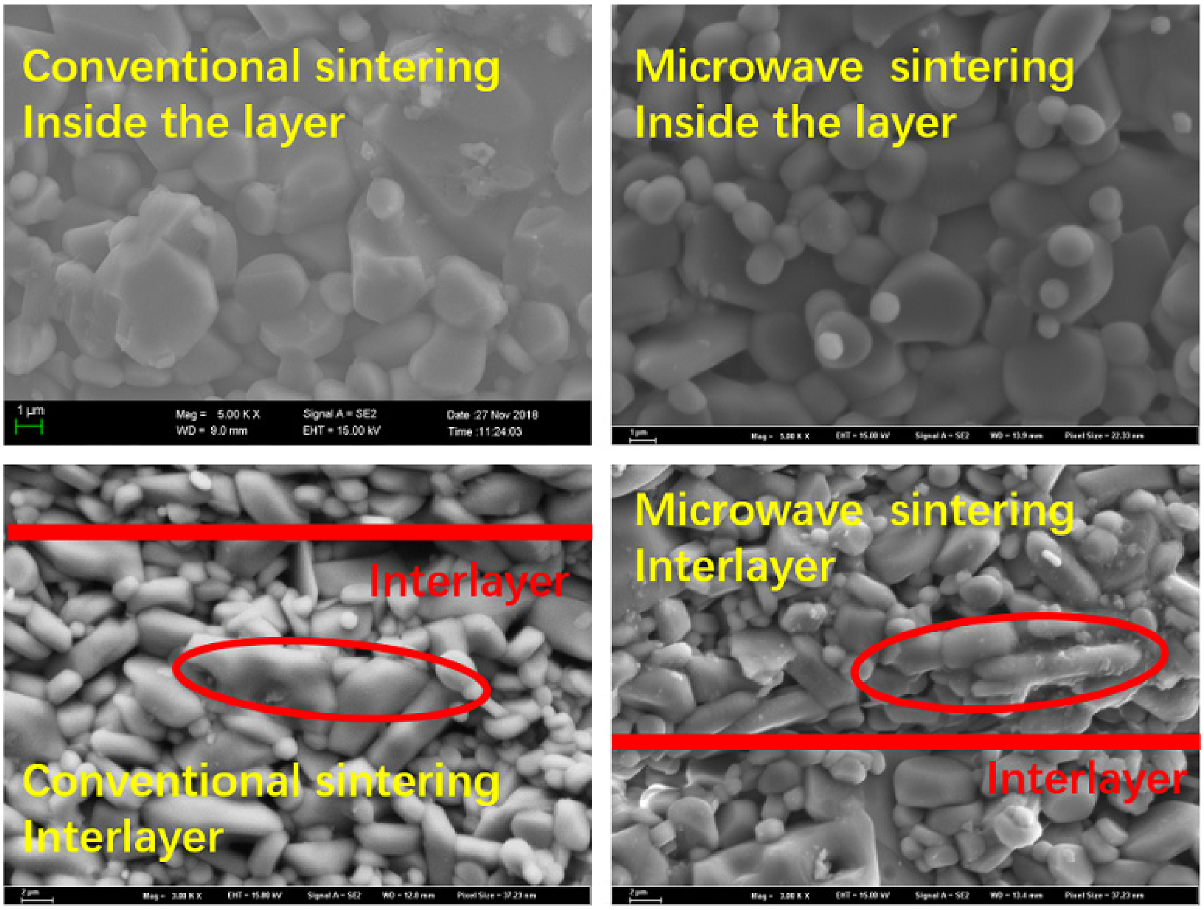
The green parts of ceramic stereolithography have the characteristics of high resin content and obvious layered structure, which put forward new challenge to the sintering process. In this paper, the effects of microwave and conventional sintering on the mechanical properties and microstructure of ceramic parts were studied at sintering temperatures of 1400 °C and 1600 °C. It is shown that, the microstructure of ceramic parts is relatively similar through both sintering technologies at temperature of 1400 °C. Comparing to interlayer, ceramic particle bonding inside the layer is more compact. Besides, there are agglomerated strip particles near the interlayer, distributing along the layering direction and blocking interlayer particle bonding. At 1600 °C, microstructure of conventional sintered ceramic part shows higher sintering degree and larger grain size, while it is finer and more uniform with spheroid grain shape for microwave sintered ceramic parts. Thus, the latter shows better flexural strength. This study shows that for the ceramic parts manufactured by stereolithography, microwave sintering has the advantages of shorter sintering time, smaller shrinkage deformation and better mechanical properties compared to conventional sintering. Therefore, it is expected that microwave sintering is a promising technology to be used to optimize the sintering of stereolithography ceramic manufactured parts.

Keywords: Stereolithography Ceramic, Microwave Sintering, Property and Microstructure



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END-LESS, CONTINUOUS AND SUPER-FLEXIBLE GLASS NANOFIBERS PRODUCED BY A NOVEL TECHNIQUE: CONTINUOUS LASER SUPERSONIC FIBERIZING

F. QUINTERO MARTÍNEZ [1], J. Penide Durán [1], A.J. Palomares-García [2], J.M. Molina-Aldareguía [2], A. Riveiro Rodríguez [1], J. del Val García [1], R. Comesaña Piñeiro [3], F. Lusquiños Rodríguez [1], J. Pou Saracho [1]

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The quest for materials with improved mechanical properties has propelled the production of high performance fibers. The development of nanofibers and nanotubes predicted the production of new nano-composites with exceptional mechanical properties. However, the breakthrough predictions haven’t been achieved jet, in part due to the reduced length of the nanofibers or nanotubes, which restrained the mechanical reinforcement and manufacturing. Consequently, there is an enormous interest in the development of advanced continuous nanofibers, but conventional methods for fiber spinning cannot produce fibers thinner than some micrometers robustly. On the other hand, the production of simultaneous strong and tough nanofibers seems to be mutually exclusive objectives. Here we present a novel and unique method to produce extremely flexible, elastic and tough (in terms of breaking energy) glass nanofibers, with diameters that range from 300 nm up to 30 µm and virtually unlimited length. The process essentially consists on heating the precursor material uniformly and extremely fast using a high power laser beam while, at the same time, the melt is rapidly stretched and cooled by the supersonic air jet. The temperature distribution must be precisely controlled by selecting the laser beam parameters in order to obtain the proper viscosity to guarantee filament stability. With this aim, an specifically conceived laser beam shaping system was designed and set-up. Concurrently, a supersonic gas flow is ejected using a de Laval nozzle expressly designed to provide an uniform supersonic air jet flowing coaxially with the filament, so that it exerts a uniform high tension along the molten material, which is essential for the rapid stretching and cooling of the filament. A suitable combination of these tools permits rapid heating, stretching and cooling of the precursor material, which is a key factor to produce fibres with small diameters, preventing filament rupture or devitrification in continuous and stable process.

This new method allows producing extremely long continuous nanofibers, virtually infinite, giving total control of diameter, and, since it is a bushing-free technique, it can be employed to process compositions with high fiber forming temperatures. In the present work we demonstrate the production of pure silica continuous nanofibers, analyze their structure and, remarkably we evaluate their mechanical properties using a set of innovative techniques. The results reveal a tensile strength of our glass nanofibers in the same order as high performance fibers, but improved toughness in the order of 100 MJ/m3 and notable flexibility attaining radius of curvature of 10 µm.

Keywords: Glass fibers, Laser materials processing, Nanofibers

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A NOVEL POROUS MULLITE AND MULLITE-Al_2O_3 MEMBRANE FOR MICROFILTRATION APPLICATIONS

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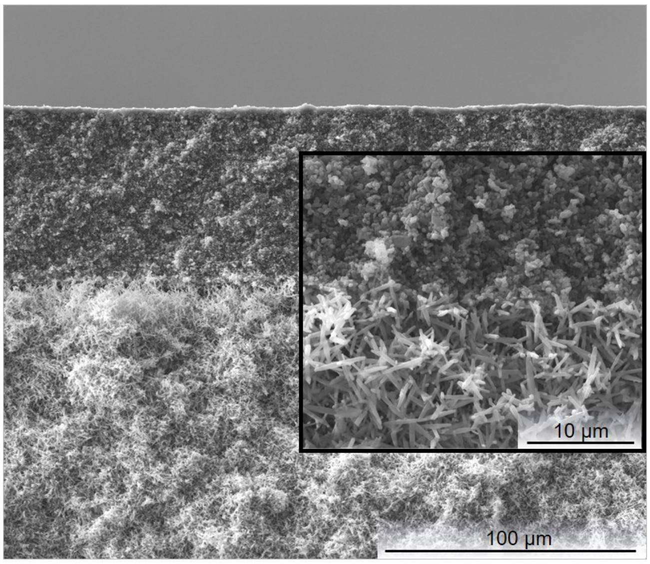
Ceramic membranes are getting increased attention these days for filtration applications because of their unique characteristics, such as high chemical stability, excellent mechanical strength, low fouling rate and long life when compared to polymeric membranes. Generally, they are prepared by partial sintering of powder compacts, forming a layered structure having different pore sizes. The primary support layer with higher pore size gives mechanical strength to withstand the pressure during filtration, followed by intermediate layers of smaller pore sizes and final separation layer on top of it. The morphology of the powder determines the final pore characteristics of the membrane. In the present study, macroporous mullite with needle-shaped interlocking crystals has been developed from China clay and AlF3.3H2O powders by a vapour phase reaction. Al2O3 has been added to the precursor powders to consume excess silica from the matrix and increase the strength of the porous network in order to use as it as a support for the membrane separation layer. The optimum combination of precursors and sintering conditions were obtained for successful support development. An α-Al2O3 separation membrane has been developed over the support by a dip coating technique, and the characteristics of the final membrane have been studied.
SEM image of the developed membrane cross-section shows that the coating of α-Al2O3 over mullite support is uniform and no cracks are found at the interface due to thermal mismatch. The support structure with interlocking needle-shaped microstructure has very high apparent porosity of 64%, flexural strength of 43 MPa, average pore size of 0.4 µm and pure water permeability of 900 L/m2.h.bar. The high permeability with a narrow pore size distribution allows direct usage of the mullite support for microfiltration applications. By using low-cost powders, lower sintering temperature and by avoiding multiple sintering procedures, the cost of manufacturing can be reduced significantly. Coating an α-Al2O3 separation layer over the mullite support helped to reduce the average pore size and surface roughness of the support without compromising the permeability much. The developed membrane has been tested for oil-in-water emulsion treatment and showed very high separation efficiency. The developed membrane material can be best suited for microfiltration applications.

Keywords: Porous mullite, ceramic membrane, alumina



SEM image of α-Al_2O_3 coated mullite membrane cross section

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DEVELOPMENT OF 3D HIGH AND LOW TEMPERATURE CO-FIRED CERAMICS PARTS BY ADDITIVE MANUFACTURING

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One vocation of the IRCER laboratory is the development of new additive processes for elaboration of 3D ceramic objects. In this respect, stereolithography has been studied. To widen the possibilities of the stereolithography, it seems interesting to study the opportunity to manufacture 3D multi-material parts, in particular of ceramic / metal type, in order to answer identified industrial needs, particularly in electronics. Currently, HTCC and LTCC (High and Low Temperature Co-fired Ceramics) parts are elaborated using two processes that are tape casting for the electrically insulating ceramic part and screen-printing for metal tracks and vias realization. The main objectives of this work are to propose a new process to obtain monolithic multi-material parts using the coupling of two additive manufacturing technologies.

In this respect, an hybrid additive manufacturing process, able to build a 3D ceramic/metal part could find a major interest in the manufacture of HTCC and LTCC electronic components. Stereolithography and micro-extrusion seem to be potential processes capable of being complementary to fulfill this objective. The advantage of using additive manufacturing instead of conventional methods is to be able to realize shapes that cannot currently be obtained in microelectronics. To straightforward fabrication of multi-material HTCC and LTCC, a strategy combining stereolithography and micro-extrusion is proposed. The model parts are 3D circuits with horizontal tracks.

Concerning HTCC, tungsten tracks with a thickness of tungsten of 30 microns between two layers of alumina have been obtain after debinding and sintering under hydrogen atmosphere. In the case of LTCC materials, the thickness of a silver track is lower and is of the order of 20 microns after debinding and sintering under the air. In both cases, their widths are between 100 and 150 microns and vias diameter between 300 and 600 microns. Thus, the parts obtained are characterized in high frequency according to several typical geometries such as resonator co-planar or in volume.

Some initial encouraging results have shown the feasibility and the complementarity of these two additive processes. Our hybrid machine makes it possible to obtain multi-material parts with quite different properties ranging from LTCC to HTCC composed of a dielectric substrate on which are deposited horizontal and vertical electrically conductive tracks. Finally, it also allows to obtain objects with complex geometries that are not possible to obtain at present with conventional process.

Keywords: Hybridization, Stereolithography, HTCC, LTCC

ABS 242

EFFECT OF PRECURSOR ON THE CHARACTERISTICS OF CERIA-BASED CERAMIC PARTICLES PREPARED BY SOLUTION SYNTHESIS

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Synthesis of ceramic powders by sol-gel techniques represents some methods to produce ultra-fine powders with suitable microstructural properties. Sol-gel techniques are classified as synthesis by liquid phase and one of the advantages is the preparation of homogeneous ceramics, concerning chemical composition. The gelling agent could have the role of propellant, complexing agent or microstructural template and they could modify the powder microstructure and create an adequate porous network which represents an important starting point for densification process of ceramics. Cerium oxide nanoparticles can be used in cosmetic products, biomedical applications, instruments and high technology, as catalysts or for preparation of dense electrolytes for solid oxide fuel cells (SOFCs) for example. The ideal ceramic process should be able to obtain ceramic powders with characteristics as morphology, particle size distribution, crystallinity and a suitable sintering, with dense ceramic samples after thermal treatment. The aim of this work is to obtain ceramic particles from solutions with different interactions among cations and gelling agent: chemical or physical interactions could be proposed. Ceria-based ceramic particles were prepared by solution synthesis using citric acid, sucrose, starch and polyethylene glicol (PEG) as gelling agents. Thermal treatment were evaluated in air at the same conditions to verify if there were different characterisitics of powder particles concerning the gelling agent. The powders were characterized by X-ray diffraction, scanning electron microscopy, N2 sorption, thermal analysis and laser scattering. The main results showed that the temperature of thermal treatment was adequate to produce crystalline phase and powders with specific surface area from 24 m2.g-1 to 75 m2.g-1 and particle size distribution at the submicron and nanometric range. This difference indicates that solution synthesis were able to tailor the morphological and surface properties, affecting particles characteristics and the microstructure of sintered dense ceramics, which could be useful to the applications of ceria based materials.

Keywords: chemical synthesis, ceria, ceramic particles

ABS 232

SOL-GEL AND ELECTROPHORETIC ALUMINA COATINGS ON METAL SUBSTRATES AS CATALYST SUPPORTS

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Catalyst supports are responsible for increasing the surface area of the active phase and increasing the mechanical and thermal strength of the catalyst. Due to to its physicochemical properties, aluminum oxide is perspective as a catalyst carrier.

The research is focused on layers made of aluminium oxide, obtained from organic and aqueous sols, deposited by two different methods which, after proper heat treatment, act as catalyst carriers.

The first method used for obtaining aluminium coating is sol-gel method, which consists in covering the surface of solids with an oxide sol and then as a result of advanced polycondensation combined with the evaporation of the solvent leading to its transformation into a gel and an oxide ceramic coating. By doing so, coatings with a thickness of less than 0.1 microns are obtained. Sol solutions are obtained from organic derivatives as a result of controlled hydrolysis and polycondensation in the presence of a catalyst. The hydrolysis of butoxy aluminum derivative was used to obtain the sol for application to metallic substrates. To draw ceramic coatings, sol is applied by means of dip-coating method with a controlled dipping and ascent rate ensuring uniform thickness. The development of the layer from the sol solution is accompanied by the evaporation of the solvent, which over time thickens and becomes more compact.

The second applied method is the electrophoretic deposition method (EPD). It involves the motion of particles of the dispersed phase in a suspension under the influence of an electric field to conductive material that is also an electrode. It leads to obtain coatings on a metal substrate, with the thickness up to several dozen micrometers. The suspension must be a stable colloidal system obtained by high solid phase fragmentation. The main advantage of the EPD method is the ability to easily and quickly obtain homogeneous layers on conductive substrates (also on the profiled surfaces). The thickness of the layers obtained can be easily controlled by changing the process conditions. So as to consolidate the layers obtained with the two abovementioned methods, thermal treatment is necessary to lead to compaction and better bonding to the substrate.

The structure (MIR, Raman) and microstructure (SEM with EDS) tests carried out showed that in both cases tight layers of aluminum oxide on steel substrates were obtained. In order to determine the nature of the surface the contact angle tests were also performed.

The conducted research allowed to state that the coatings obtained by means of electrophoretic depositions are characterised by better adhesion to the substrate. They present great homogeneity and higher thickness than sol-gel coatings. Contact angle tests indicate that both coatings are hydrophilic. The obtained materials are extremely promising because of their physicochemical and surface properties.

Keywords: Aluminum oxide, Electrophoretic deposition, Sol-gel method

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THERMAL PROPERTIES OF DENSE AND POROUS, Si-BASED POLYMER DERIVED CERAMICS

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The thermal properties of Si-based polymer derived ceramics (PDCs) are studied in this work. Ceramic foams and thin-disks, having the basic chemistry Si-C, Si-O-C, and, Si-O-N-C were developed via a modified template replica and casting technique respectively, followed by controlled pyrolysis. Porous ceramic foams having densities in the range 0.03 gcm-3- 0.56 gcm-3, having a range of porosity from ~74% to 98% and dense disks with bulk density in-around 2.0 gcm-3 were used for the study. The dense samples were also produced with different amount of free carbon in order to explore its role on the thermal properties of PDCs. The developed artifacts are characterized to study the basic features, primarily investigating the thermal properties, viz. thermal conductivity, thermal expansion, etc. of the material. A Gibson-Ashby modeling to explain the thermal conductivity of the porous ceramics was also attempted.

Polyurethane (PU) templates were used to develop the porous ceramics, while the thin disks were obtained by casting the precursors on a mylar sheet. Polycarbosilane, polysiloxane, or, polysilazane was used as the precursor based on the chemistry required. The precursor impregnated monoliths and thin disks were pyrolyzed also in controlled atmosphere at a maximum temperature in the range 1200 – 1500 °C.

The PU templates and the polymeric precursors were systematically studied using spectroscopic techniques to understand the basic chemistry. The obtained ceramics were found to be thermally stable up to a temperature of 1500 °C (in Argon). The RT thermal conductivity (TC) measured using hot disk method for the reticulated ceramics (foams) were found to be in the range 0.03Wm-1K-1- 0.25Wm-1K-1. The TC of the dense ceramics (disks), measured using laser-flash technique, will also be discussed in comparison with the TC estimated from the Gibson-Ashby model. The Cfree effect on the dense properties will also be thoroughly investigated for the different systems considered.

Keywords: Reticulated foams, Ultra -light, Low thermal Conductivity

ABS 196

SELFPROPAGATING HIGH TEMPERATURE SYNTHESIS AND STUDY OF HIGH-ENTROPY CERAMICS BASED ON THE CARBIDES OF REFRACTORY METALS

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The purposes of this work are to obtain, and study high-entropy alloys and ceramics based on the compositions of the resulting alloys by methods of high-energy ball milling (so-called mechanical alloying or synthesis) and consolidation by spark plasma sintering.
High entropy materials by definition contain five or more basic elements with a concentration of 5% to 35%. They are usually characterized by a wide range of properties and are a very promising area for research and applications [1]. The equimolar composition of HfTaTiZrNbMo was studied in [2] and showed high strength properties at room temperature and up to 1200 ° C. High-entropy alloys (HEA) are obtained as a rule by arc melting. However, this kind of production leads to the formation of a dendritic structure, which leads to a deterioration in mechanical properties. To fix the fine-grained structure of the material, powder metallurgy is a best way. As a new class of high-entropy materials, Jian Luo et al. [3] presented a diboride based on the Hf-Ta-Ti-Nb-Mo-Zr system under investigation, which has properties in excess of the high-temperature material. In this work, the material was obtained by a combination of high-energy ball milling, selfpropagating hightemperature synthesis (SHS) and consolidation in a spark plasma sintering unit. Therefore, it was decided to conduct a study of this system, obtaining a high entropy ceramic (HEC) based on this alloy.
To produce the reaction mixture, high-purity metal powders Hf, Ta, Ti, Nb, Zr, Mo (> 99%) and graphite (99.8%) were used. To obtain HEA powders of metals were processed on a ball planetary high-energy mill for 90 minutes, and then for 5 minutes with the addition of carbon. Then the SHS reaction was carried out, and a bulk material was obtained by sintering in a spark plasma sintering (SPS) and hot-pressing (HP) machines.
Ball milling of powders made it possible to obtain an amorphous structure, even after joint millig with carbon there was no formation of monocarbides or other carbides. As can be seen from Fig. 1, after the SHS, a mono-phase with an FCC lattice was formed. The material produced by SHS and SPS demonstrated higher hardness as compared to the specimens produced by mechanochemical synthesis and hot pressing, reach values up to 26 GPa with a combination of SHS and spark plasma sintering. It can be assumed that the resulting high entropy ceramic will have superior mechanical properties.

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Keywords: High entropy ceramic, SHS, Refractory carbide

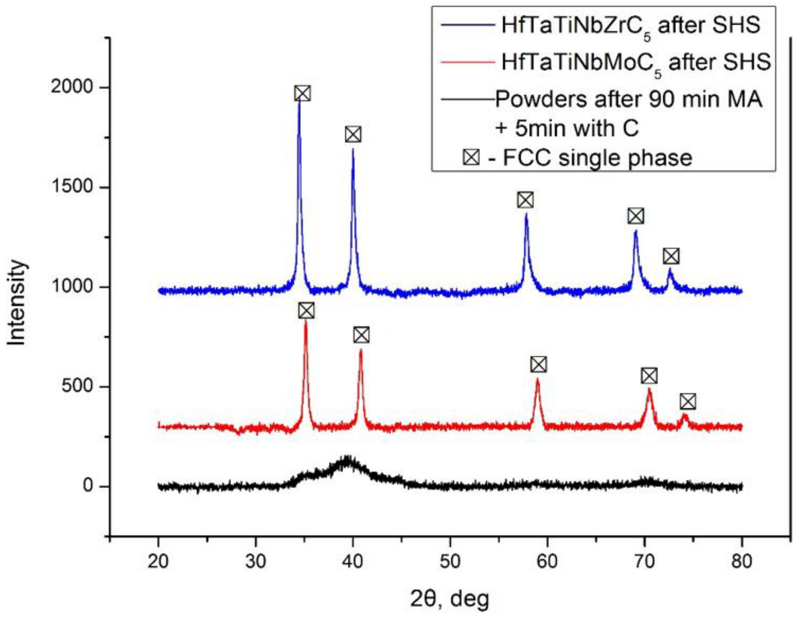

Figure 1 - Results of XRD analysis powder of HEC after ball milling and SHS

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SiOC CERAMICS WITH OPEN AND PARTIALLY CLOSE POROSITY

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Porous SiOC ceramics were fabricated by using open and partially open polyurethane foams (PUFs) and preceramic polymers. The used preceramic polymer blend was prepared by dissolving PHMS (Polyhydridomethylsiloxane), PDMS (Polydimethylsiloxane) and TMTVS (2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane) in acetone PHMS:PDMS:TMTVS by 1:1:0.08 weight ratio. Platinum-divinyl-tetramethyl-disiloxane complex (having 0.05 vol% Pt) in xylene, was added prior to the foam impregnation. The impregnated PU foams were cured at different temperatures ranging from room temperature to 220°C, and then pyrolyzed under Ar atmosphere at 1000°C. The curing process was found to be crucial factor determining the strut characteristics, meaning that it is possible to form both dense and hallow struts. The specific surface area of the foams was found to be dependent on the PDMS ratio and could reach around 75 m2/g. All manufactured samples were characterized in detail by various structural techniques namely; SEM, XRD, TGA, FT-IR, RAMAN and finally for mechanical properties by Cold Crushing Strength (CCS).

Keywords: porous ceramics, polymer derived ceramics, silicon oxycarbide

ABS 184

SOL-GEL-DERIVED POWDERS AND SUSPENSIONS FOR TREATMENT PLANTS

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Nanoparticles are actively used in the different fields of science and technology. Recently, there was reported in several studies that using some types of the nanoparticles for the seed processing and for the processing during vegetation can be promising for the increasing plant resistance tor the different stress factors protection (drought, heat, frost, UV). Nanoparticles with photocatalitic and magnetic properties are considered in the first place. Interestingly, there are two opposite points of view regarding this prospective among the researches. Some researchers believe that nanoparticles are really easily assimilated by the plants in comparison with more conventional forms of fertilizers, like soluble salts or complex compounds. Others, on the contrary, consider these nanoparticles toxic and less effective. Examples of successful use of silica sols and nanoparticles TiO2, Fe2O3, etc. for treating seed and plants are known. The beneficial effect of TiO2 is revealed in the fact that communities of beneficial bacteria form around them, increasing the resistance of plants to infections. The possibility of using magnetic nanoparticles in agrotechnologies has been explored only in recent years. In this report, sol-gel synthesis of the silica sol based suspensions containing TiO2 or diamond batch, as well as aqueous suspensions of iron oxides particles will be described. These suspensions were used for pre-sowing seed treatment of spring barley and Chinese cabbage in order to protect seeds and seedlings from pathogens and provide them with essential nutrients. The state of the seeds surface was studied by the SEM and EDX with respect to the conditions of the synthesis of sols and suspensions (pH, TEOS content and organic modifiers, aging time). Phyto-tests for Chinese cabbage and spring barley of various varieties were carried out. The influence of sol-gel treatment on the growth characteristics of seedlings, the numerical composition of epiphytic microorganisms on the seeds surface and the resistance of plants at the early stages of their development to the phytopathogens have been established. After the treatment, with TEOS-derived sols mixed with organic polyols and TiO2 nanoparticles, the number of mycelial fungi, including potentially pathogenic, on the surface of barley seeds reduced. On the contrary, the number of bacteria of ecological-trophic groups potentially useful for plants increased. It was noted the stimulation of seed germination, growth and development of seedlings. The report will also present the first results of experiments on the treatment of seeds and plants with sols and suspensions with magnetite and maghemite nanoparticles.

Keywords: sol-gel technology, nanopowders, agrotechnologies

ABS 183

3D PRINTED ORGANIC-CERAMIC COMPLEX HYBRID STRUCTURES WITH HIGH SILICA CONTENT

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3D printing enables one-step fabrication of objects with high geometrical complexity. The recent interest in 3D printing has led to the development of novel ink compositions which enables obtaining objects with improved performances and functionalities. Among the current 3D printing technologies, Digital Light Processing (DLP) printing which is based on localized photopolymerization, enables formation of 3D structures with both high complexity and resolution, at high processing speed, without the need for support materials.

Here we report on a new hybrid organic-inorganic ink for DLP printing, which can undergo both polycondensation and radical polymerization. The ink composed of silica based UV-curable oligomers was prepared by a sol-gel method, which yields 3D objects with high silica content, and thus superior properties. The printed monolithic objects have a glossiness similar to silica glass, light weight and are crack free. They have also excellent mechanical strength compared to currently used high performance polymers (139 MPa), have a very high stability at elevated temperatures (Heat Deflection Temperature >270 °C), and high transparency (89%).

The new hybrid ink fills the gap in additive manufacturing of objects composed of ceramics only and organic materials only, thus enabling harnessing the advantages of both worlds of materials.

Keywords: 3D printing, sol-gel, DLP

ABS 174

PRESSURE CONTROL OF ABLATION LAYER COMPOSITION, NANOPARTICLES SIZE AND PHASE SYNTHESIZED BY PULSED LASER ABLATION IN SUPERCRITICAL CARBON DIOXIDE

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Titanium dioxide (TiO2) has been a material of great interest in the scientific community as well as industry after its excellent photocatalytic properties were reported by Fujushima and Honda in 1972 [1]. TiO2 has a band gap at approximately 3 eV, and thus requires blue or UV light to be active. There have been significant efforts to increase the absorption in the visible range. Thakur et al. reported production of nanomaterials of dopant free multiphase titanium oxides with increased absorption in vis-NIR region and average band gap of 2.39 eV [2,3]. They attributed the decreased band gap due to the presence of multiphase titanium oxide phases. To synthesize unagglomerated nanoparticles consisting of multiphase titanium oxides or create a thin layer of such material on target surface is rather difficult. In our recent study, we demonstrated the synthesis of well-dispersed multiphase titanium oxide nanoparticles by pulsed laser ablation in supercritical carbon dioxide, the results of which are currently in publication process. In this study, we further investigate the effect of CO2 pressure on the nanoparticle size, phase and size distribution as well as on the composition of ablated layer on target surface.

In this study, we used a 1064 nm wavelength fiber laser operating at 101 kHz repetition rate to cause ablation on titanium target surface which was fitted inside a high pressure chamber. The target was surrounded by pressurized CO2 with pressures from 50 up to 400 bar at 50 °C. Above a pressure and temperature of 73.9 bar and 31.1 °C respectively, CO2 exists in its supercritical state. Transmission electron microscope (TEM) was used to study the nanoparticle size and morphology while Raman microscopy and x-ray diffraction (XRD) were used for phase analysis of nanoparticles and laser ablated surface. Additionally, scanning electron microscopy was used to characterize the ablated target surface. TEM image analysis for average nanoparticle size showed that from 50 to 150 bar pressure, the particle size remained almost same ~20 nm while at 200 bar, it dropped slightly followed by a surge at 400 bar to ~23 nm. XRD indicated presence of multiphase titanium oxides both in nanoparticles and ablated layer on the target but the presence of titanium carbides was only indicated for the ablated layer. This suggested decomposition of CO2. Further results from this study will be shared at our oral presentation at ECerS 2019 Turin.

To the best of our knowledge, this is the first study to report the effect of CO2 pressure from 50 bar gaseous state up to 400 bar supercritical state on the size, morphology, and phase of titanium oxide nanoparticles and on composition of laser ablated layer. As it is the first report of this study topic, it is important to present it through an oral presentation at ECerS 2019 in the symposia 'Innovative processing and synthesis' under nanostructured ceramics / powder synthesis / thin films and coatings / novel forming methods.

Keywords: Pulsed laser ablation, multiphase titanium oxide, supercritical CO2

ABS 165

DEVELOPMENT OF SUBSTITUTED β-TCP FOR IMPROVED THERMAL STABILITY DURING MICROWAVE SINTERING

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This project concerns the synthesis of doped β-TCP and the fabrication of ceramics parts by robocasting intended for medical applications. β-tricalcium phosphate (β-TCP, β-Ca3(PO4)2) is one of the most attractive biomaterials for bone repair since it shows an excellent biological compatibility, osteoconductivity, and resorbability. Due to its interesting properties, it can be used to produce bone implants serving as temporary supports for bone regeneration. However, when heating, β-TCP presents a phase transition to α-TCP at 1150°C which occurs with a large lattice expansion causing microcracks and reducing shrinkage during sintering with as consequence a sintering temperature limitation. This phase transformation is a drawback for the use of new sintering methods like flash sintering, spark plasma sintering or microwave sintering. Indeed, these processes present a difficult control of the temperature but also advantages as very short thermal treatment durations and close control of the grain growth. Thus, it could be interesting to increase the thermal stability of β-TCP to use these rapid sintering processes without the formation of α-TCP.

A possible solution is to dope the β-TCP with cationic dopant(s) during the synthesis to increase its thermal stability and prevent the phase transformation. Therefore, the aim of this work is to increase the sintering temperature of β-TCP above the typical allotrotropic transformation temperature by cationic dopant addition in order to reach higher relative density value and higher mechanical properties. Moreover, cationic dopants can also improve biological properties of β-TCP as bone implant.

For this purpose, the β-TCP is synthetized by coprecipitation of Ca(NO3)2 and (NH4)2HPO4 solutions under controlled temperature and pH. The dopants are added into the reagent solutions to optimize the substitution. Complete characterizations are conducted to evaluate the influence of these dopants on the thermal stability and biological properties of β-TCP powders. In addition, conventional and microwave sintering are compared in terms of microstructural and mechanical properties.

This PhD is part of the DOC 3D Printing project supported by the H2020-ITN-MCS program that is a consortium of European universities and industrialists around the additive manufacturing of ceramics. This project aims to cover the additive manufacturing of ceramics from the development of the raw material to the testing of marketable products for the health and aerospace industries. With a budget of € 3.5 million financed by the European Union, 6 academic partners, 7 industrialists and the standards certification association in the field are working together to develop this research area.

Keywords: Beta-TCP synthesis, cationic doping, microwave sintering

ABS 161

EFFECT OF Ta_2O_5 ADDITION ON MICROSTRUCTURE AND OPTICAL PROPERTIES OF $MgAl_2O_4$ CERAMICS PREPARED BY REACTIVE AND NON REACTIVE SPARK PLASMA SINTERING

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The magnesium aluminate spinel MgAl2O4 is considered for extensive applications as an ionizing radiation resistant optical material. The appropriate MgAl2O4 ceramics have to possess simultaneously a high mass density and small grain size at the nanoscale. In this work, the effect of a grain growth inhibitor Ta2O5 on microstructure and optical properties of MgAl2O4 ceramics has been investigated. The ceramics were prepared by non-reactive and reactive spark plasma sintering. Two precursor materials were studied : commercial MgAl2O4 powders and stoichiometric mixture of Al2O3 and MgO synthesized via an original method of α-Al2O3 nanopowder liquid impregnation with Mg(NO3)2. Correlated structural, microstructural and spectroscopic (transmission and cathodoluminescence) analyses were carried out. It was observed that a tantalum rich phase is formed and segregates onto the grain boundaries leading to a bimodal grain size distribution, while providing a moderate inhibition of the grain growth. The intensity of the principal ultraviolet emission (4 - 6 eV) of the spinel was suppressed after Ta addition.

Keywords: Nanostructured MgAl2O4 ceramic, Inhibition of grain growth, powder synthesis

ABS 152

EFFECT OF SURFACE TREATMENT ON THE DISPERSION OF NANO ZIRCONIA PARTICLES IN NON-AQUEOUS SUSPENSIONS FOR STEREOLITHOGRAPHY

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Stereolithography (SLA) can be used to fabricate ceramics with highly complex architectures. However, the ceramic stereolithography process require the creation of stable and well-dispersed ceramic suspensions with high solid loading. In addition, the relationship between cure depth and exposure energy is important, which significantly influences the dimensional accuracy and properties of final parts. It is a key step to optimize the relationship between cure depth and exposure energy.

Nanozirconia powder doped with 3 mol% yttria was chose as the ceramic material, whilst the UV-curable resin consisted of Acryloyl morpholine (ACMO) and Polyethylene glycol diacrylate (PEGDA) with the addition of Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO). Stearic acid (SA), oleic acid (OA), Disperbyk (BYK), 3-glycidoxypropylthrimethoxysilane (KH560) and variquat CC (CC) were selected as the dispersants.

Sedimentation tests can estimate the effect of dispersants on the stability of the ceramic suspensions. The particle size distribution (PSD) was measured using dynamic laser scattering (DLS) with a Brookhaven ZetaPlus Particle Size Analyser (USA). The Fourier transform infrared (FT-IR) spectra of the dispersants, as-received zirconia powders and treated zirconia powders were obtained using FTIR spectrometry. The rheological characteristics were determined using a rotational viscometer. The microstructure was observed using a field emission scanning electronic microscope.

BYK, KH560 and OA all showed superior results compared to the SA and CC, with less settling being observed from sedimentation tests. Moreover, the BYK was the most effective dispersant and 3 wt% of it could effectively disperse the nanozirconia particles to a D50 of ~50 nm. FTIR spectra indicated that the BYK was successfully coated on the surface of zirconia powder. A zirconia part was fabricated using the modified suspension. After sintering, a significant shrinkage was measured (21.9% in X-Y plane and 28.9% in Z directions); the SEM image showed the sintered part offered a high level of densification.

Keywords: Dispersants, Zirconia suspensions, Stereolithography

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ALIGNMENT OF TUBAL PORES IN CERAMICS BY MAGNETIC-FIELD ASSISTED COLLOIDAL PROCESSING

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Porous materials are used in a wide variety of applications, such as absorber, separator, medium for cellular culture. Boron carbide is usually used as the neutron absorbing materials, but cracks are easily generated during operation because of volume swelling due to the accommodation of helium gas during the neutron absorption reaction. Releasing the accumulated helium is very important for avoiding the crack generation, but it is difficult because a conventional pellet has few closed pores, 5~10%, without specific direction. In this study, in order to release the gas easily, alignment of the tubal pore was controlled by the strong magnetic field-assisted colloid processing. Reagents used in this study were B4C as the base particles, Nylon 66 (N66, nominal shape ϕ 10 x300 μm) as a pore former, and polyethylene Imine (PEI, Mw: 10,000) as a dispersant. Slurries including boron carbide powder, Nylon 66 and PEI was prepared via planetary mixing and ultrasonication. The slurry was consolidated by slip casting on a turntable placed at the center of a horizontally-setup 12 T magnetic field. After the slurry was poured into a porous alumina mold, the stage was kept turning at various conditions until a consolidated cake was formed. After burning off N66, the matrix of B4C was densified by Spark Plasma Sintering at 1700C for 3min, 75 MPa in an Ar atmosphere. In microscopic observation, uniformed dispersion of N66 and excellent alignment were observed in the obtained B4C green . Besides, the c-axis orientation of matrix phase B4C was indicated from the XRD analysis. We achieved simultaneously to control the crystalline orientation of B4C and align the pore-forming agent by controlling the dispersion of particles in a slurry and the rotating condition of a magnetic field. After burning off N66, alignment of the residual tubal pores was observed. After densifying by SPS, the textured B4C with the oriented tubal pore can be obtained from this green compact. This ceramic is constructed with oriented tubal pore-phase, and dense- c-axis alignment B4C phase.

Keywords: orientation, colloidal processing, strong magnetic field

ABS 146

REACTIVE SYNTHESIS, MICROSTRUCTURE, AND PORE-SIZE CONTROL OF OXIDE-BASED SPHERICAL POROUS GRANULES

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Spherical porous granules (SPGs) are promising for many applications, e.g., heterogeneous catalysts, catalyst supports, drug delivery carriers, healing of defective bones and so on. A variety of processes have been developed to form SPGs; they are mostly liquid-based processes, particularly spray drying, suspension hardening, drop-in-oil, sol-gel granulation and freeze-granulation. Solid-based processes are rarely realized for the SPG production, except the mechanical granulation method with a rotating fluidized bed.

Recently, we have developed a new solid-based process to synthesize SPGs by a one-step heat-treatment of the MgCO3(basic)-alpha-Fe2O3-Nb2O5 mixed powder. Pseudobrookite-type MgFeNbO5 SPGs with 3-D network structure, typically 50-100 micrometer in diameter, were successfully obtained.

To expand practical applications of SPGs, the pyrolytic reactive granulation process should be expanded to a variety of functional double oxides, e.g., spinel-, perovskite-, pyrochlore-type oxides. Here, we present our recent development of new groups of SPGs as well as some functions, e.g. durable vapor release.

Keywords: Spherical porous granule, Reactive sintering, Nanoporous materials

ABS 144

HIGHLY POROUS OXIDE CERAMIC AS THE SUPPORT FOR CATALYSTS

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Porous oxide ceramics were obtained by suspension casting technology in which pore has been formed in result of chemical reaction of metallic aluminium and water in the basic medium. Cordierite and alumina ceramic has been chosen as basic materials for use as a support for catalysts and simultaneous filtration of liquids and catalytic decomposition of organic pollutants. 5% nano-scale powder of silicon carbide and zirconia for the cordierite ceramic or 5 % of microcrystalline cellulose spheres with a diameter of 300 and 600 µm for the alumina ceramic were used as additives to improve the pore structure. Cordierite ceramic was sintered at 1250 to 1350°C, but alumina ceramics at 1500 to 1700°C. Pore structure: porosity, pore size distribution, specific surface area and permeability has been chosen as the more important properties for the ceramic filter. Pore structure was determined using mercury porosimetry (PoreMaster Quantachrome Instrument) and nitrogen adsorption method (Quantachrome Instrument Nova 1200e). The high-resolution scanning electron microscope FEI Nova NanoSEM was used for the investigation of the materials structure. The extraction-pyrolysis method was used for the obtaining of few transitional oxides catalysts coatings on the sintered ceramic. The grain size in the catalyst coatings were determined by atomic force microscope (AFM) VEECO CP II. Activity of catalysts was characterised with water oxidability or chemical demand of oxygen (CDO) in the water solution of phenol depending on the solution temperature and duration of catalysis. CDO was determined by the photometric method (Aqualytic® photometer-system AL200 COD Vario with thermoreactor AL125).

Three separate pore size distribution areas were determined for the obtained ceramic samples regardless of the composition and sintering temperature. The pore volume in these areas changes depending on the sintering temperature. The silicon carbide and zirconia additives were influenced the pore size distribution and specific surface area both in the micrometers and nanometers scale. Pore structure of cordierite ceramic obtained using nanopowders additive was changed in result of formation of zircon or small crystals of secondary mullite in the larger pores depending on the initial composition. Cordierite and alumina ceramics depending on the pore structure were chosen as filter materials and were used for the coating with catalysts. Nano-scale and micro-scale particles of catalysts were formed direct both on the surface and in the pores of support material. The specified catalyst grain size ranges from 90 nm to 200 nm and depends on the pyrolysis temperature and number of coatings.

Keywords: oxide ceramics, pore structure, support for catalysts

ABS 136

STRUCTURAL AND ELECTROCHEMICAL CHARACTERIZATION OF COBALT-CONTAINING CARBONS DERIVED FROM CARBIDES THOUGH CHLORINE ETCHING

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Nowadays, the demand for resources is growing constantly due to the development and growth of the world population. In this way, energy is one of the most essential resources for the human being. The huge demand for energy implies in some cases the import of it, and its generation still can not be separated from polluting activities such as the burning of fossil fuels.

For that, renewable energies are responsible for carrying out a transition from the current energy model to a sustainable one that is able to meet the demand energetic. Batteries, capacitors and fuel cells have a series of characteristics that can still be improved and that give them with great interest.

In this work, highly porous carbon materials have been synthesized for being used as electrodes in supercapacitor devices focused in achieve higher capacitance values. Carbon materials were prepared from the commercial polymer SMP-10 and Cobalt (II) 2,4 pentanedionate. This is a metallic compound that is expected to increase the storage capacity through redox reactions. Divinylbenzene has also been added in order to increase the carbon content in the final material. The materials obtained by pyrolysis in N2 atmosphere at different temperatures, were treated in a chlorine gas flow for removing silica. The carbons derived from carbides (CDCs) were characterized by different experimental techniques like Infrared Spectroscopy, X-ray Diffraction, Raman Spectroscopy, Differential Thermal and Thermogravimetric analyses, Nitrogen Adsorption and Scanning Electron Microscopy.

The electrochemical properties were studied by Cyclic Voltammetry and Chronopotentiometry. The capacitance values improve considerably after leaching with chlorine gas increasing from 2 F/g up to 40 F/g. Such capacitance values are in the range of active carbons used commonly in this kind of research. However, the addition of Co does not produce pseudocapacitance phenomena may be due to that Co are neutralized by C inhibiting redox reactions.

Keywords: Polymer Derived Ceramics, Carbon, Electrochemistry

ABS 129

DEVELOPMENT OF A NUMERICAL SIMULATION MODEL FOR PREDICTING THE STIFFNESS OF CERAMIC PARTS PRODUCED BY STEREOLITHOGRAPHY

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The control of the mechanical properties of green parts produced by stereolithography is an important aspect to take into account in the manufacturing process. Stiffness has to be monitored in order to properly manufacture and clean parts.

This study aims to develop numerical simulation of curable ceramic systems to predict the Young's Modulus of green parts depending on the manufacturing parameters. This model is validated by experimental Young's Modulus measurements by coupling a tensile test with a Digital Image Correlation technique. This experimental approach is conducted on a commercial photopolymerizable Al2O3 paste. A design of experiments is used to reduce the number of experiments. Therefore, the influence of manufacturing parameters on the stiffness of the parts is investigated.

The simulation model enables to predict the Young's Modulus for each experiment with a maximum error of 6.1%, which makes it valid. Moreover, it allows to highlight that Young's Modulus measurements of green parts using an optical method is highly effective. The simulation model also provides visualization of the exposure distribution and the scattering phenomenon, which has to be considered, especially for ceramic systems. Finally, the robustness and the accuracy of the simulation model is confirmed with its validation for another ceramic system, for an organic photopolymerizable system and for another stereolithography device.

Keywords: Stereolithography, Numerical Simulation Model, Young's Modulus

ABS 115

MODIFICATION OF THE BAND GAP AND THE PHOTOCATALYTIC POTENTIAL OF TITANIA NANOPARTICLES BY DOPING WITH CERIA

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Nowadays, titania nanoparticles (TiO2NPs) are of great interest in various fields of research, mainly due to their high surface area / volume ratio and excellent thermal, mechanical and photocatalytic properties. Precisely, due to their good photocatalytic activity they have been successfully incorporated in air and water treatment devices and catalysts and catalyst supports. However, the photoactivity of TiO2NPs is limited to the UV-region, and solar energy is not enough since only 5% of sunlight has a UV-region. Due to the above, several investigations have been carried out in order to extend its spectrum of optical absorption (band gap) to the visible region and thereby achieve an improvement in photocatalytic efficiency. To date, several strategies have been used to achieve this objective, among which is the modification of the stoichiometry of titania by doping with ions or rare earth oxides, which according to various improves the structural stability and photochemical response of the material. Therefore, in the present work, ceria-doped titania nanoparticles in different molar proportions were synthesized by the sol gel method assisted by a microemulsion of reverse micelles. According to the results, the incorporation of ceria in the titania lattice significantly reduces the average diameter of the nanoparticles and modifies the intrinsic structure of the activation band was found, finding values of band gap slightly corrected to the lower energy band (visible-region), and significantly improved the photocatalytic effect on the degradation of methylene blue, as model molecule.

Keywords: ceria-doped titania nanopartic, photocatalytic activity, band gap

ABS 112

ELABORATION OF AN ALUMINUM OXIDE THIN FILM DEPOSITED BY MAGNETRON SPUTTERING ON BORON NITRIDE SUBSTRATES: ROLE OF THE PHYSICAL AND CHEMICAL PROPERTIES OF BN SUBSTRATES

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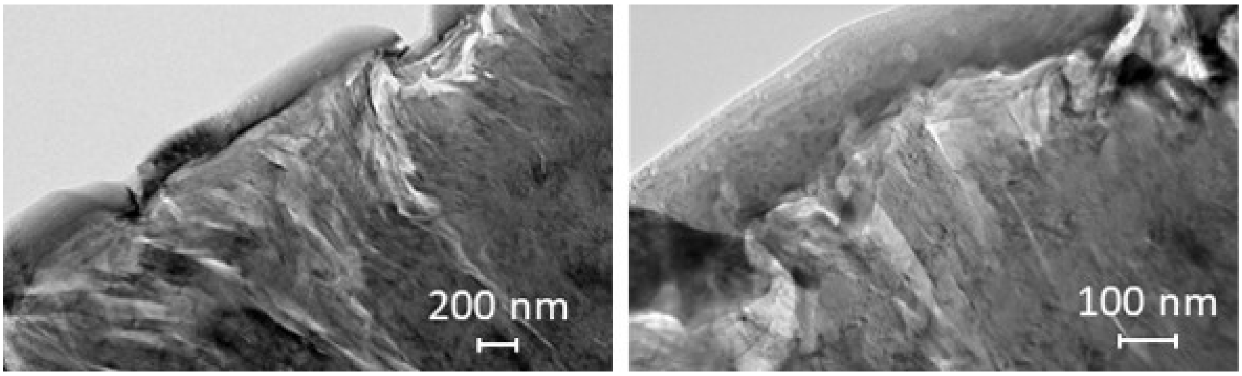
Boron nitride is a non-oxide ceramic exhibiting excellent thermal and chemical stability. This compound exists in various crystallographic structures, the most common being hexagonal (h-BN) and cubic (c-BN). The surface of this material can be protected from wear by a hard-ceramic compound like aluminum oxide. In this study, aluminum oxide films were deposited on boron nitride substrates by magnetron sputtering. The aim of this work is to evaluate the quality of the interface between these two materials. To do so, the first step was to control the process parameters like the target power, the working pressure and the substrate bias, in order to determine their influence on the deposition rate, on the thin film structure, and on the chemical composition.

The use of the two different substrates (h- and c-BN) has also allowed studying the role of the physical and chemical properties of BN substrates on the adhesion of the alumina thin film. The roughness and the surface state of the substrates have been characterized by XPS, optical profilometry, XRD and SEM. It was found that the roughness average of the surface is around 1.48 µm ± 0.12 µm and the elements detected by XPS were boron (37.6 ± 1.3 at.%), nitrogen (47.2 ± 0.9 at.%), oxygen (4.9 ± 0.2 at.%) and carbon (10.3 ± 2.0 at.%).

Finally, the role of an annealing treatment on the structural properties of the alumina coating and on its adherence has been investigated. This heat treatment has been performed at 1200°C in vacuum. After annealing, the Al_2O_3 – BN system has been evaluated using XRD, SEM, XPS, TEM. The interface between the BN substrate and the Al_2O_3 film was observed by TEM. The corresponding cross section of the h-BN – Al_2O_3 system (see Fig. 1) clearly shows that there is no interface formation between the substrate and the coating.

Keywords: Magnetron Sputtering, Boron nitride, Aluminum oxide



ABS 109

UREA-GLASS PREPARATION OF TiN/TiO$_2$ COMPOSITE NANOPARTICLES FOR ORGANIC DYE ADSORPTION AND PHOTOCATALYSIS

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Titanium nitride (TiN), titanium oxide (TiO2), and their composite nanoparticles have been prepared by a facile urea-glass method involving use of urea as the nitrogen source and metal chloride as the powder precursor at a relatively low temperature of 800 oC in nitrogen atmosphere. Crystlline phase and bandgap energy of the composites can be tailored by adjusting the urea/metal mole fraction (R) and niobium (Nb) doping in the precursor stage. As R increases from 1 to 6, the composites change from predominately crystalline TiO2 to pure TiN, together with a minimum bandgap energy of ca. 2.4 to 2.5 eV at R = 3 to 4 for the TiN/TiO2 composites. Dye adsorption under dark situation and photocatalytic degradation of methylene blue (MB) in water under visible light irradiation have been examined. The presence of TiN in the composites appears to render a pronouncedly enhanced adsorption of MB dye molecules, due partly to the increased specific surface area of the particles. The adsorption exceeds 90% for the TiN particles with R = 6 and specific surface area of 227.5 m2/g at a relatively short time (90 min) under dark situations. In addition, the Nb doping facilitates both the dye adsorption and photocatalytic MB removal under visible light irradiations. The degradation of MB dyes in water is the most pronounced (ca. 17 to 19% for 120 min illumination) when the composites are of the minimum bandgap energy with R = 3 to 4; to which, the absorption edge extends to ca. 500 to 520 nm of the visible-light region.

Keywords: Composite, Nanoparticle, TiN/TiO2

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FIELD ASSISTED PROCESSING OF ADDITIVE MANUFACTURED ADVANCED CERAMICS

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Advanced ceramic products for highly demanding applications in electronics, energy, healthcare and defence sectors require densification/sintering, a high temperature process (~1000–2000oC) that in industry can take days. The amount of energy needed, and CO2 emitted, is therefore very significant. Conventional processing of these functional devices/components are often plagued by interfacial issues, unwanted grain growth and limitations of co-firing dissimilar materials. Thus, rapid and efficient sintering methods such as SPS, Microwave Assisted Sintering (MAS) and Flash Sintering (FS) are continuously being developed. These approaches referred as Field Assisted Sintering Techniques (FAST) use an external field that was demonstrated to have a positive effect on densification. For example, the FS method, for reasons that are far from fully understood, has yielded full densification in very short periods (5 s) at very low furnace temperatures (850oC) for zirconia, and at a surprisingly low temperature of 325oC for Co2MnO4 spinel ceramics. The associated time and energy advantage is estimated to be staggering, as well as the ability to tailor the microstructure. In this talk, we will have a closer look at MAS and FS methods– one a well-established and the other a newly emerging densification method. The MAS method can be suitable for the processing of various simple and complex shaped engineering components, the early use of FS method was restricted to dog-bone shaped ceramic specimens – that are both difficult to make and do not have much industrial applicability. However, the recent developments have demonstrated that FS can also be used to sinter different sample shapes. We investigated the feasibility of sintering of 3D printed BaTiO3 based PTCR heaters, ultra-low loss 5G microwave dielectrics, YSZ/ZTA biomedical components using MS and FS methods along with measurements of shrinkage and thermal mapping. This talk will review these developments on FS along with the operative mechanisms in comparison with MAS.

Keywords: Additive Manufacturing,Flash Sintering,Microwave Processing

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SiOC ADSORBENTS FOR CATIONIC DYE REMOVAL

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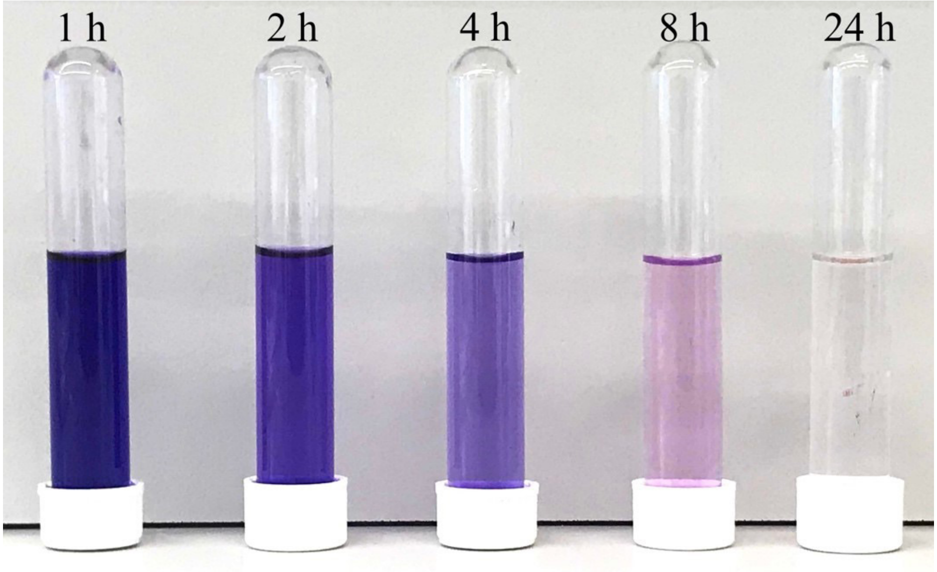
Objective To produce highly permeable SiOC ceramic foams by using preceramic polymer blends by simple one-pot blending technique, and test those porous materials as cationic dye (methylene blue (MB), Rhodamine B (RB), and Crystal Violet (CV)) adsorbent from aqueous solutions.

Materials & methods All the starting chemicals were used as received: vinyl-terminated polydimethylsiloxane (PDMS), 2,4,6,8-tetramethyl-2,4,6,8- tetravinlycyclotetrasiloxane (TMTVS), polymethylhydrosiloxane (PHMS) , Platinum - divinyltetramethyldisiloxane complex including blends were mixed with a weight ratio of 1/0.055/1/0.055, cured and pyrolyzed. Obtained bodies were first HF etched, and characterized in depth. Following that and all the adsorption studies were carried out by using both batch and column adsorption techniques.

Results & Conclusions Following the etching by HF, the surface area enhanced from below 5 m2/g to above 770 m2/g. While the experimental data were fitted to both Langmuir and Freundlich models, the Freundlich isotherm did not provide a good fit instead Langmuir model showed decent agreement with data. It is observed that the adsorption capacities increased at least 6 times upon etching. Regeneration studies were followed both by medium temperature heat treatment (causing dye decomposition) and leaching by ethanol, and even after 3 re-loading cycles, SiOC foams demonstrated higher than 97% retention. These samples produced by inexpensive and very simple method could find applications where purification of contaminated water is needed in harsh environments.

Keywords: dye, adsorbent, porous SiOC



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MAGNETIC FIELD ASSISTED FILM DEPOSITION OF MULTI-FUNCTIONAL LAYERED DOUBLE HYDROXIDES SYNTHESIZED WITH HIGH-POWER SONICATION

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Layered double hydroxides (LDH) exist as natural 2-D structures of general formula of [MII1-xMIIIx(OH)2] x+(Ay-)x/y·zH2O. They are composed of alternating positively-charged mixed metal MII-MIII hydroxide layers and interlayers occupied by anions (Ay-) and water molecules. The metal cations in the layers are coordinated by six oxygen atoms and these oxygen octahedra are edge-linked. Functionality of LDH can be extended by means of inclusion of specific cations, in particular, magnetic ones.

The main method of synthesis of LDHs is co-precipitation from aqueous solutions followed by anion exchange, the method being rather direct and yet, reproducible, however it is slow and water-consuming. In this work, an alternative to co-precipitation is evaluated. High-power ultrasounds are applied in sonocrystallization of Co/Al LDH with the main purpose of reducing from hours to minutes the time necessary to create a homogeneous crystallite size and increasing crystallization efficiency. In addition, the crystallites of LDH from sonocrystallization were found to have little agglomeration.

The study of recently prepared LDH with different CoII/AlIII cation ratios revealed a behavior of the magnetic susceptibility with broad transitions at 75 K and 175 K. It was notice that the Curie – Weiss linear approximation of the inverse magnetic susceptibility on temperature is different in the paramagnetic ranges above and below the anomalies. Analysis of the magnate transitions suggests reducing of ferromagnetic interactions between cobalt ions with decreasing temperature.

In frame of the observed magnetic behaviour, results of a first time study on deposition of LDHs particles on substrates under a magnetic field oriented either in-plane or perpendicular to substrates of different types are presented by the , the objective being continuous and uniform films with electrochemical response and magnetic anisotropy.

Keywords: Sonocrystallization, Layered double hydroxides, Film deposition

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STEREOLITHOGRAPHY AND POLYMER-DERIVED CERAMICS, PRECURSORS OF Si(O)C

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Silicon Carbide (SiC) is known as a high performance ceramic used in harsh environment. Dense SiC with high mechanical properties is conventionally obtained by pressing, machining and sintering around 2000°C. The machining step is therefore expensive and geometries to be addressed are limited. Additive manufacturing (AM) processes offer the opportunity to manufacture complex parts. Among the AM, the stereolithography (SLA) process based on photocurable resins is known to shape ceramics parts. SiC powder absorbs the UV light blocking the resin photopolymerization, even at low solid rate (<10%vol). Polymer derived-ceramics (PDC) such as polycarbosilane and polysiloxane are Si(O)C precursors and do not absorb the UV light. The objective is then to develop a UV-photocurable PDC resin and manufacture SiOC parts by SLA.

Stereolithography of PDC materials consists in mixing a UV-curable resin with PDC. The crosslinked resin confer the required strength to obtain green parts. Then a pyrolysis is performed to remove the organic phase through an appropriate thermal treatment. Parts have been manufactured on the M120 Prodways equipment.Thermogravimetric analyses were performed to evaluate the ceramic yield in respect to the preceramic polymer content. Chemical analysis were carried out to measure Silicon, Carbon and Oxygen concentrations of pyrolysed PDC. X-ray diffraction was performed to identify the conversion temperature into SiC and its phase polytype.

Polymethylsiloxane (Silres MK), polyvinylsiloxane (Silres H62C) and phenylmethyl polysiloxane (Silres H44 - Wacker Chemie) are PDC with high ceramic yield conversion (>50% wt). The Si, O, C concentration of the ceramic material pyrolysed at 1000°C under Argon depends on the methyl, phenyl, vinyl groups in the polysiloxane (Figure a and b). From the element concentration and the formulation retained SiC_(x) O_(2-2x) + y Cfree, SiC, SiO_2 and free-C rates are calculated. Following this methodology, and regarding the XRD analyses, PDC can be ranked in function of their SiC contents, the SiC-polytype phase and the crystallization temperature (Figure c).

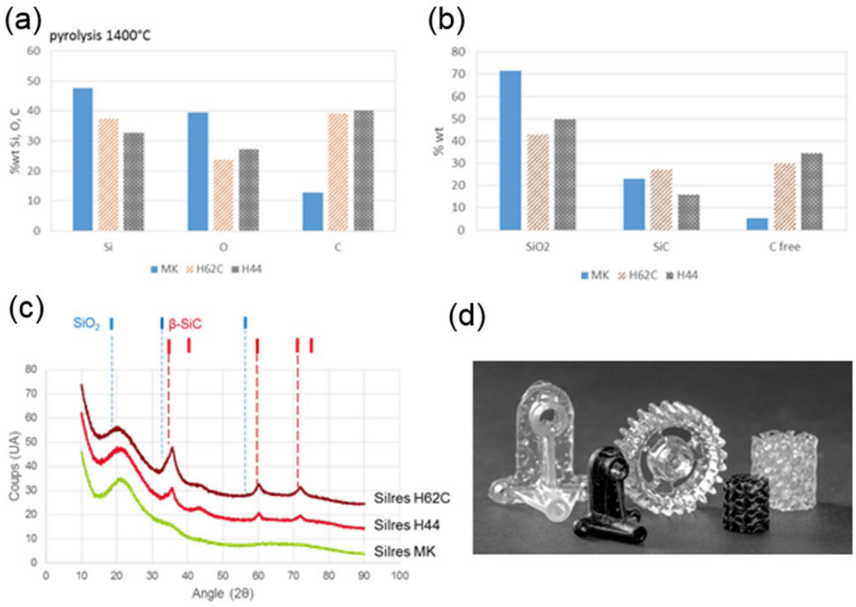
Liquid PDC (H62C), which is miscible in photocurable resin are suitable for SLA. These formulations are time-stable in terms of reactivity and viscosity, compared to formulations based on solid PDC dissolved in a solvent (H44 and MK).

From these investigations, Si(O)C parts have been manufactured by SLA (Figure d).

This paper presents investigations on UV-curable PDC for stereolithography process. It includes characterizations of the PDC, like temperature decomposition (phase, gas) and ceramic conversion rate, the development of a SLA resin and parts manufacturing.

Further investigations will be presented.

Keywords: Ceramic additive manufacturing, Polymer derived-ceramics, Stereolithography



(a) and (b) PDC pyrolysed at 1400°C under Ar – (a) Si, O, C concentrations; (b) SiO2, SiC, free-C concentrations
(c) XRD – PDC pyrolysed at 1000°C under Argon
(d) Si(O)C parts before and after pyrolysis

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DENSIFICATION AND CRYSTALLOGRAPHIC ALIGNMENT OF DIRECT WRITTEN PIEZOELECTRIC CERAMICS PRINTED WITH ANISOTROPIC NOZZLES

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The additive manufacturing of piezoelectric ceramics facilitates increased flexibility of crystallographic alignment directions. Direct write additive manufacturing is of interest for this purpose due to the generation of shear stresses during the printing process. Shear stress, and the subsequent torque it produces, aligns anisotropic template particles which nucleate crystallographically oriented grains upon densification of the ceramic . The quality of alignment between these template particles and the resulting grains, as well as the final sintered density, directly influences the piezoelectric response of the ceramic . This study explores the effect of shear field profile, controlled by changing the geometry of the printing nozzle, on the alignment of anisotropic barium titanate template particles in Pb(In1/2Nb1/2)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 paste and the subsequent densification of the printed ceramic bodies. Increasing the aspect ratio of the printing shear field facilitates increased alignment quality and textured volume fraction compared to previous low aspect ratio attempts. The effect of shear field and paste rheology on green density gradients around template particles and between printed filaments will be related to the densification and geometric fidelity of the sintered ceramic shapes. Ultimately, through control of the profile and magnitude of printing shear stresses, as well as the paste rheology, the direct writing of dense, textured Pb(In1/2Nb1/2)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 ceramics will be demonstrated.

Keywords: Direct writing, Templated grain growth, Sintering

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JOINING OF ALUMINA CERAMICS BY SPONTANEOUS-COAGULATION-CAST CAKE

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Recently we found alumina slurry prepared by a dispersant PIBM (a copolymer of isobutylene and maleic anhydride) spontaneously gelled at room temperature in air. It has been demonstrated that many ceramic systems could be shaped by PIBM. Based on this, a new technique for the green state joining of alumina ceramics without paste has been developed. The joining process involves integrating two wet green bodies cast by PIBM in a gelling state, followed by drying and sintering. For example, wet green bodies after aging 10 h were joined, and the joint region of the dried and sintered sample exhibited a homogeneous microstructure without an interlayer. The flexural strength of the joined sample (468.5 ± 62.9 MPa) was nearly equivalent to that of a monolithic sample (470.6 ± 27.4 MPa). The joining mechanism was discussed on the basis of interaction among PIBM molecular chains. The proposed joining technique is simple and promising for producing advanced ceramics with large sizes and/or complicated shapes.

Keywords: Spontaneous-coagulation-cast, PIBM, joining

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MECHANICAL PROPERTIES OF COMPLEX ZnO STRUCTURES USING NANO-LEVEL 3D PRINTERS

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ZnO is one of the representative metal oxide semiconductors with large natural abundance and exhibits special physical and chemical properties. Applications of ZnO as a n-type semiconductor to into light emitting devices (LEDs), solar cells, detection devices, functional devices, etc. are progressed. Structure control of ZnO is important for enhancing device performance.

In this paper, we focused on two photon polymerization, which is one of molding processes, as a method for fabricating complex ZnO structures.

In this method, a photoresist was selectively cured by inducing a two-lattice excitation phenomenon by an ultrashort pulsed laser to form a three-dimiensional(3D) microstructure having monolithic nanosized grains. It can fabricate 3D structures which is several 10um resolutions. However, the main problem is it only can fabricate polymer structures.

Therefore, the purpose of this research is to focus on mixing a photoresist with an organic solvent (EMOD) containing a metal organic compound, and to directly create a micro ZnO structure using a two-lattice excitation method. The precondition is: mixed photoresist optically transmit laser wavelength at 780nm, and absorb half wavelength at 390nm. Analysis of reaction in the mixed photoresist was carried out.

In order to investigate the applicability to this process, we tried to prepare a microstructure by adjusting the EMOD fraction of the mixed photoresist. Experiments were also conducted to evaluate the mechanical properties of the structure.

The experiment was conducted by changing the mixing ratio of photoresist and EMOD. As a result, when the EMOD was 40vol.% or more, the structures could not be formed. This is thought to be because the formation of the network structure of the photoresist was inhibited. However, with the composition of 40vol.% or less, it was possible to form 3D structures with a line width of 1.25um. Furthermore, we succeeded in synthesis of ZnO 3D structures by heating at 400°C for 1 hour.

From the above results, it revealed that this method is suitable for formation of 3D structures of functional ceramics.

Keywords: ZnO,3D printer, Mechanical properties

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3D-PRINTED LIGHTWEIGHT CERAMICS USING CAPILLARY SUSPENSIONS WITH INCORPORATED NANOPARTICLES

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Capillary suspensions can be used as stable precursors to create porous ceramics with a high open-porosity. Capillary suspensions are solid-liquid-liquid systems with a small amount of an immiscible secondary fluid added to a suspension. A strong particle network forms due to capillary forces, which changes the material strength from fluid-like or weakly elastic to strong gel-like behavior [1]. This strong particle network controlled by capillary forces does not collapse during debinding or sintering, and therefore can serve as precursor for sintered materials with high open-porosity [2].
We utilize the secondary fluid to deposit ceramic nanoparticles specifically in the contact regions of the microparticles. Therefore, we have advanced control over the resulting microstructure while harnessing the nanoparticles as sintering aids. Based on this concept, the mechanical strength is increased up to 5 times and the limit for the maximum obtainable porosity is pushed to 75 %, still preserving a high level of mechanical strength. Thus, we demonstrate state-of-the-art mechanical properties without sacrificing versatility and tunability. Combination with a 3D-printing (DIW) process yields cellular structures with specific strength close to that of balsa wood. For a relative density of 0.3 we achieve a compressive strength of 60 MPa, doubling typical values for cellular ceramics at this relative density. We reach these values for two raw materials, Al2O3 and aluminosilicate, strongly differing in strength, indicating the methods independency of the used chemical compositions and strengthening its versatility. Furthermore, we can use the nanoparticle-laden secondary liquids as a temperature stable "bonding agent" for catalytically active particles, e.g. zeolites, to generate an additional hierarchical level. The sintering activated neck formation of the ceramic nanoparticles "glues" the coarse particles together and supplies mechanical stability while preserving the inherent porosity in the catalytic particles. Therefore, we can manufacture hierarchically structured porous monoliths with high specific surface area for high-temperature catalytic applications. The fully open, tunable porous structure and applicability to a wide range of sintering materials offers the possibility to meet requirements for targeted lightweight high temperature processes, e.g in biomedical, filtration, energy storage, heat exchange, gas adsorption, insulation or catalytic applications.

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Keywords: Open Porous Ceramics, Direct Ink Writing, Lightweight materials

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HIGHLY POROUS LANTHANUM ZIRCONATE CERAMIC FOAMS WITH ULTRA-LOW THERMAL CONDUCTIVITY AND HIGH STRENGTH

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Lanthanum zirconate ceramic foams with ultra-low thermal conductivity and high strength have been prepared using sodium dodecyl sulfate (SDS) as particle stabilizer. The wet foams stabilized by lanthanum zirconate particles are ultra-stable due to the partially hydrophobic particles modified by SDS. Lanthanum zirconate foams exhibit close cells with thin cell wall and small grain size. Lanthanum zirconate ceramic foams with porosity of 95% have compressive strength of 0.65 MPa. Decreasing solid loading leads to the increase of porosity of ceramic foams. The compressive strength was enhanced significantly by increasing the sintering temperature. Lanthanum zirconate ceramic foams with porosity of 95% has low thermal conductivity of 0.051 W(m.K)-1, which is a promosing material for high temperature insulation applications.

Keywords: porous ceramics, lanthanum zirconate, thermal conductivity

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OPTIMIZATION PROCEDURE FOR CERAMIC ADDITIVE MANUFACTURING BASED ON DIGITAL LIGHT PROCESSING

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As is well known, Additive Manufacturing (AM) comprises the use of layer-by-layer manufacturing in order to build a part by the addition of material. AM is perceived as a sustainable and a key emerging technology for lower energy consumption and more efficient production.

Potential advantages of such a manufacturing approach include a reduction in material waste, production of high added-value final parts and products, etc. These technologies are capable of processing a wide variety of materials, polymers, metals and ceramics. In the case of ceramics

One of the most commonly used AM technologies for ceramics is Mask Image Projection based on Stereolithography (MIP-SL). MIP-SL, also called Digital Light Processing (DLP) using DLP projectors, run a Frontal Photopolymerization Process (FPP).

A common issue with AM technologies based on FPP is the uncontrolled penetration of light energy into the photocuring material. FPP analytical models allow obtaining printing parameters for a successfully printing process, such as the photocuring conversion ratio of the photocurable material that determine Young's modulus or density, among others, in the final parts.

The use of ceramic particles modifies the FPP parameters in DLP due to absorption and light scattering of the particles. The higher refractive index difference between particle and resin, the stronger the light scattering, hence a reduction of cure depth.

An analytical optimization method for MIP-SL based on a finite element discretization is presented and implemented in order to minimize the difference between the objective and the achieved photoconversion ratio of printed parts to improve resolution and z accuracy.

The FPP material parameters are obtained through experimental tests, such as the increase of material attenuation factor on account of ceramic particles in the photocurable resin. Furthermore, numerical simulation based on FPP analytical models is used to determine the printing parameters which optimize the printing process in terms of photocuring conversion ratio.

Keywords: Analytical optimization method, Additive Manufacturing, Ceramics

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SIZE REDUCTION EFFECTS OF CRISTOBALITE AND α-Al_2O_3 POWDERS ON SYNTHESIZING MULLITE

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Size reduction effects of the starting powders on mullite formation in the cristobalite / α-Al2O3 systems were examined. Cristobalite and α-Al2O3 powders of D50 200, 300, and 400 nm were mixed in a stoichiometric composition of mullite, 3Al2O3•2SiO2 (71.8 wt% α-Al2O3 and 28.2 wt% SiO2) respectively making the starting powder systems. The mixtures then thermally treated up to 1300oC --1600oC range to form mullite. Size reduction effects were evaluated using differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM) techniques.

The activation energy calculated by isothermal experiments shows the size reduction of cristobalite powders experienced more impact on the generation of mullite than that of α-Al2O3, being the main factor determining the reaction. These results indicate that the amorphization of cristobalite may trigger the reaction of SiO2 with α-Al2O3, initiating the nucleation of mullite. The mullite formation is related to the amorphization of silica. Cristobalite powder amorphized in advance during the thermal treatment that promotes the Si component migrates to contact the α-Al2O3 particle to form mullite. The amorphization temperature decreased with the size reduction of α-Al2O3 particles Thus, the temperature of initiating mullite formation seemed to be lowered by size reduction of α-Al2O3. A size reduction in cristobalite powders accelerated the amorphization rates and resulted in higher rates of mullite formation, lowering the temperatures at which the powder systems converted entirely into mullite. These results indicate that α-Al2O3 particles can act as the hosts for mullite formation and determine the particle size of mullite as well. The crystal orientation of the mullite was controlled by the α-Al2O3 matrix, that is, [001] α-Al2O3 to [001]mullite.

Keywords: Powder synthesis, Mullite, Alumina

ABS 937

WHY SOFT PROCESSING (=LOW-ENERGY PRODUCTION) OF ADVANCED CERAMICS IS DIFFICULT BUT NECESSARY FOR SUSTAINABLE SOCIETY?

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Modern our society has been developed with various advanced materials. Most of advanced materials, Metallurgical materials, Semiconductors, Ceramic materials and Plastics have been used in wide area of applications. Most of them except for bio-polymers & bio-minerals have never been produced via Biological systems. Thus they have generally been fabricated artificially and/or industrially by so-called high-technology, where high temperature, high pressure, vacuum, molecule, atom, ion, plasma, etc. have been used for their fabrications, then consumed huge amount of resources and energies thus exhausted huge amounts of wastes: materials, heats and entropy. They are completely against Biological system based upon Water Cycle in Mother Nature. Considering the lowering of total energy consumption and wastes, we have challenged to fabricate those advanced inorganic materials with desired shape/size/location, etc. directly in low energetic routes using (aqueous) solutions since 1995 an innovative concept and technology, “Soft Processing” or “Soft Solution Processing”. In addition to several oxides, the preparation of Graphene and functionalized Graphene under ambient temperature and pressure conditions will be talked.

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EFFECT OF NANO CARBON SOURCES ON THE MECHANICAL PROPERTIES AND PORE CHARACTERISTICS OF MESO-MACRO POROUS SIC SYNTHESIZED BY DIRECT REACTION OF SILICON AND CARBON

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In this study, the meso-macro porous SiC was synthesized by a direct reaction between Si and C at the temperature below 1300 Celsius degrees. Carbon black powder (50 L, N774), and carbon black / CNT mixed powder were used as the starting carbon source material. Si powders with size of 1 um were used as starting Si source material. Carbon and Si sources were mixed by ball milling process using ethanol solution. The mole ratio of carbon to silicon was varied from 1.0 to 2.5 and the amount of CNT used was varied 0 to 30 wt% of the total carbon source. The green bodies were prepared by a uniaxial pressing method, and then heat-treated at a temperature range of 1100 to 1250 Celsius degrees for 10 hours under an argon atmosphere. In this study, the effects of carbon source as well as carbon/Si mole ratio on the pore characteristics and mechanical properties of synthesized meso-macro porous SiC. With increasing synthesis temperature, the amounts of residual Si was found to be significantly reduced. Any residual Si was not observed in porous SiC using various C/Si mole ratio synthesized at 1250 Celsius degrees. It was found that the average pore size of the synthesized porous SiC by a direct reaction between Si and C was varies from 50 nm to 10 um. The porosity and surface area of synthesized porous SiC were found to be closely related to the carbon source used as starting material. As the molar ratio of carbon in the starting material was increased, the porosity and surface area of synthesized porous SiC was increased slightly, but the compressive strength of synthesized porous SiC was significantly decreased. The size of the carbon black powder did not affect the porosity, but the compressive strength of the porous SiC decreased with increasing the size of the carbon black powder. It was found that application of CNT as a carbon source improve the pore characteristics as well as the compressive strength of synthesized porous SiC.

Keywords: SiC, Porous ceramic, meso-macro pore

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FABRICATION AND MECHANICAL PROPERTIES OF POROUS Si_3N_4 CERAMICS PREPARED VIA SHS

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Porous silicon nitride ceramics were directly prepared by self-propagating high temperature synthesis (SHS) process. The phase compositions and microstructures are sensitive to the compositions of the starting materials due to the rapid reaction and sintering process. The effects of Si3N4 diluent and Y2O3 sintering additive were investigated. The XRD patterns and SEM microstructures proved the samples with 63wt.% Si3N4 diluent could provide appropriate temperature and pore~channel for the fabrication of long rod-like~Si3N4 porous Si3N4 ceramics. A porosity of 40%~47% and a flexural strength of 118~216MPa were gained after SHS with different Y2O3 content. The thermal shock results indicated that strength retention kept stable in the temperature difference of 800oC.

Keywords: Si3N4, prorus, faom

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PREPARATION OF HIGH-PERFORMANCE POROUS CERAMICS VIA FOAM-GELCASTING METHOD

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Elongated mullite self-reinforced porous ceramics, MgAl2O4 porous ceramics, porous Si3N4 whiskers bonded/reinforced SiC ceramics, and hierarchically pore-structured porous diatomite ceramics were prepared by foam-gelcasting technique. The flexural strength of elongated mullite self-reinforced porous ceramics with porosity of 67.0% was about 27% higher than these counterparts without elongated mullite, and HMOR at 1473 K of the former (6.7 MPa) was about 13.6% higher than that latter (5.9 MPa). Porous MgAl2O4 ceramics with a porosity of 75.1% and an average pore size of 266 micron had a compressive strength as high as 12.5±0.8 MPa and thermal conductivity as low as 0.24 W/(m•K). As-prepared Si3N4(w)/SiC porous ceramics with 71.53% porosity respectively had flexural and compressive strengths of 5.60±0.69 MPa and 12.37±1.05 MPa. The hierarchically pore-structured porous diatomite ceramics containing 84.5% porosity and having compressive strength of 1.1 ± 0.07 MPa showed the lowest thermal conductivity of 0.097 ± 0.001 W/(m•K); after Co-modifying by graphene and carbon nanobelt, lotus seedpod bioinspired 3D superhydrophobic diatomite porous ceramics were fabricated, the as-prepared porous ceramics which can continuously separate oil from oil/water mixture demonstrated 3-30 times higher adsorption capacity of oil/water separation than conventional inorganic sorbent materials, and their compressive strength is about 70-270 times higher than that sponge/graphene based sorbent materials.

Keywords: Foam-gelcasting, Porous ceramics, Mechanical properties

ABS 12

LOW TEMPERATURE MOLTEN SALT MEDIATED SYNTHESIS OF BORON-CONTAINING CERAMIC POWDERS

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Because of their superior properties such as high melting point, high mechanical strength/hardness/elastic modulus, good thermal conductivity, excellent wear resistance, outstanding chemical resistance, and relatively low density, boron-containing ceramics such as metal borides (e.g., ZrB2. HfB2, and TiB2) and boron-based carbides (e.g., B4C and Al8B4C7) are used extensively at both low and high temperatures in many important sectors, including armour, aerospace, machinery, thermal management, refractories, and nuclear reactors.

A number of methodologies/techniques have been used to prepare these powders with different shapes and sizes, including carbothermal or borothermal reduction and self-propagating high temperature synthesis, which unfortunately suffer from various disadvantages, in particular, requirement of high synthesis temperature, use of expensive raw materials and heavy agglomeration of the final product powder.

To address the issues, the present have developed a novel molten salt mediated synthesis technique, with which a range of high quality boron-containing ceramic powders can be prepared at much lowered temperatures.

The raw materials were mixed with a low melting water-soluble salt/salt assembly, and contained in a crucible which was then fired at different temperatures (> the melting point of the salt) for different time periods. After firing, the reacted mass was washed repeatedly with hot water to remove the residual salt. The resulting product powders after drying were characterised in detail by using different techniques such as XRD, SEM and TEM. Based on the results, the effects of different processing parameters such as starting powder composition, salt type/assembly/amount, firing temperature and time, and amount of reducing agent on the quality of product powder (in particular, purity, morphology and size) are discussed and the corresponding reaction mechanisms clarified.

Several important types of binary and ternary boron-containing ceramic powders, including ZrB2, HfB2, TiB2, Al8B4C7, MoAlB, TiB2-Al2O3, and ZrB2-SiC were synthesized by using this molten salt mediated technique, and compared with those resulted from the conventional synthesis routes. Our results showed that the synthesis temperatures generally can be reduced to 1000-1250oC, much lower than used by the conventional synthesis techniques. For example, in the cases of TiB2 and Al8B4C7, the synthesis temperature was reduced to as low as 1000 and 1250oC, respectively. Sizes of the product powders also can be readily tailored/controlled. In most cases, nanosized or submicron sized product powders were obtained. Apart from single phase borides, boron-containing composite powders (e.g., TiB2-Al2O3, and ZrB2-SiC) can be similarly synthesized. The above results were attributable to the molten salt medium which facilitated the reaction processes via two main mechanisms, “dissolution–precipitation” and “template formation”.

Keywords: Molten salt synthesis, Boride, Mechanism

S02

HT PROCESSES AND ADVANCED SINTERING

INVITED LECTURES

ABS 792

COUPLED EXPERIMENTAL AND NUMERICAL INVESTIGATION OF EVOLUTION OF ANISOTROPIC MICROSTRUCTURES DURING STRESS-ASSISTED SINTERING

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In many cases, a porous body is subjected to non-hydrostatic stresses during sintering. Experimentally and using multi-scale, we show that the pore shape evolution during stress assisted sintering is dependent on the size of the pore. We define two types of pores – intrinsic small inter-particle pores, and extrinsic significantly larger than the intrinsic pores. We present experimental results on the development of pore shape anisotropy during sintering under uniaxial stresses of ceramics containing both type of pores. The effect of applied stress on the microstructure is investigated. As expected during sintering under non-hydrostatic stress, the pore shape becomes anisotropic and the pores orient preferentially. However, the intrinsic pores preferentially align parallel while the extrinsic pores align perpendicular to the applied stress. For both intrinsic and extrinsic pores, the degree of anisotropy increases with applied stress, reaches a maximum and then decreases with further increase in stress. Applied stress leads to finer grain microstructures at a particular density. Multiscale numerical simulations provide insights into the origin of this behavior. Based on these results, we also provide a fundamental definition of the transition pore size – pore size at which the behavior changers from intrinsic to extrinsic.

Keywords: stress-assisted sintering, anisotropy, microstructure evolution

ABS 941

DISCRETE ELEMENT MODELING OF SINTERING HETEROGENEOUS STRUCTURES

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For numerical modeling of sintering process on the microscale the discrete element method (DEM) can be effectively used. The investigated material is represented as a set of interacted primary particles. This allows to reproduce structures of heterogeneous materials consisting of several components or material with complex geometries.

In this contribution the application of DEM on thermal barrier coatings (TBC) is discussed. The TBC are highly porous structures with three-dimensionally highly-ordered macro pores, also called inverse photonic crystals. In experiments they show crack formation, delamination and opening of the structure due to sintering effects although an application as TBC requires stable macroscopic mechanical, photonic and structural properties at high temperatures.

Simulation case studies show differences in material transport within the structure leading to the formation of defects, e.g. initial cracks on the surface and within the structure at the struts. Besides this shrinkage, deformation of pores occur as well as shrinkage of the whole structure in vertical direction. To simulate mechanical properties of sintered materials and possible crack initiation and propagation the bonded particle model (BPM) is applied. The BPM is an extension of DEM, where the material is represented as set of primary particles connected with solid bonds.

The influence of different parameters like initial relative density or macro pore arrangement was investigated and compared with results of experiments to obtain deeper understanding of the process.

The authors gratefully acknowledge financial support from the German Research Foundation (DFG) via SFB 986 “M^3”, projects A3 and C5.

Keywords: Discrete Elemen Method, Heterogeneous Structures, Mechanical Strength

ABS 942

JOINING AND INTEGRATION OF CERAMICS

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Innovation in processing and characterization of advanced ceramic-based joined components developed at GLANCE-Glasses, Ceramics and Composites research group at Politecnico di Torino, Italy (www.composites.polito.it) will be presented and discussed.

Joined components for several applications such as automotive, aerospace, energy production (nuclear fusion and fission, solid oxide cells and concentrated solar energy), also in the form of sandwich structures have been designed, fabricated and characterized in simulated working conditions: recent results on each topic will be briefly reviewed.

The combination of advanced design of interfaces and joining materials/technologies, selective matrix removal from the composite surface, laser structuring and mechanical machining of the composite/metal surfaces will be discussed and compared to existing solutions.

The work done with the aim of developing reliable and user-friendly international standard test to measure the shear strength of joined components will be reviewed.

Finally, J-TECH@POLITO, a recently funded Advanced Joining Technology interdepartmental research center at Politecnico di Torino, will be described together with collaboration actions and opportunities for common research activity on joining.

Keywords: JOINING,CERAMICS,COMPOSITES

ABS 400

FREE AND PRESSURE-ASSISTED MICROWAVE SINTERING: TOWARDS TRANSPARENT $MgAl_2O_4$ CERAMICS

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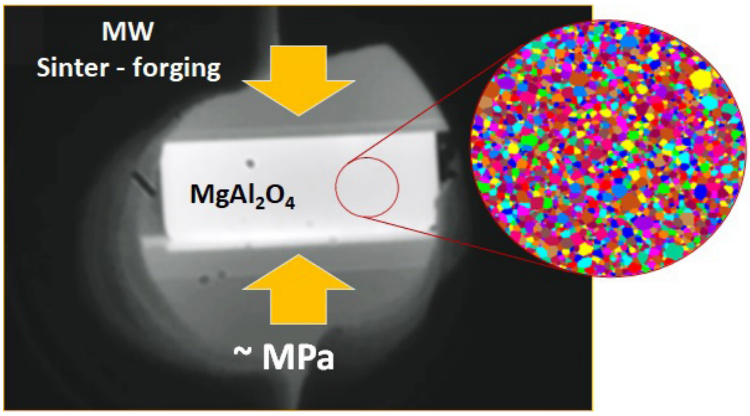
Objectives Over the years, microwave energy has emerged as an efficient source of heating for material processing. This technology provides a rapid and a volumetric heating of the material, which can be very attractive for controlling microstructure on sintered materials. However, this technology still needs to be improved in terms of temperature regulation in order to achieve a satisfactory reproducibility while controlling the final product microstructure. In particular, for obtaining transparent MgAl2O4 ceramics, it is of primary importance to remove all the porosity and to maintain the grain size as small as possible with a homogeneous distribution. Usually, transparent spinel material is successfully produced when pressure-assisted sintering (HIP, SPS, etc.) is used for removing the residual porosity. Therefore the objectives of this work are to depict our latest developments for controlling the overall microwave process (temperature regulation and heating distribution), with and without applied pressure, in a view of producing highly transparent MgAl2O4 ceramics.
Materials and Method Green compacts of spinel were produced by slip casting for having high quality green materials. An original 915 MHz single-mode cavity fully automatised was developed in order to control the heating cycles and the temperature distribution within the material. An analogy of the microwave process with a simple electrical circuit was made to better understand the key parameters that allow controlling the overall process. In addition, a uniaxial press was adapted to a 2.45 GHz single-mode cavity for developing an original microwave sinter forging process. Both systems were used to sinter spinel materials. The sample microstructures were subsequently characterised in terms of grain size, microstructure homogeneity, density, hardness and transparency.
Results Two main results were obtained. First a very unique microwave single-mode cavity, working at 915 MHz was fully developed. Highly dense materials (>95%) were sintered with remaining close porosity. It has been shown that after subjecting those materials to a Hot Isostatic Pressing stage, highly transparent materials were obtained. Second, the microwave sinter-forging process was shown to be very promising for producing transparent spinel material without using HIP process, in a very short amount of time in air (<30 min).
Conclusion An original microwave sinter-forging process was developed to produce full dense transparent spinel in air. Otherwise, important improvements of the microwave system were made, increasing significantly the technological maturity of the microwave process.

Keywords: microwave sintering, sinter forging, transparent ceramic



ABS 307

MATERIAL MODELS FOR DIGITAL TWIN OF CERAMIC PROCESSING

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A digital twin refers to a set of physical process (such as sintering) and its digital representation (such as a finite element model for sintering). It is a natural extension to computer modelling that has been made possible by the abundant availability of low cost and fast in-process measurement and data collection. A key difference between conventional computer modelling and digital twin is that the computer models on the digital side of the twin are frequently updated and revised using the data collected from the physical side of the twin. The key advantage of this approach is to reduce uncertainty in the computer models. Uncertainties in both the structure and parameters of material models (such as sintering mechanisms and anisotropy) have been a major challenge in computer modelling of ceramic processing. Unconventional processes such as 3D printing of green bodies provide new challenges because it is not possible to perfect the corresponding material models for small patch production. The update and revision of material models in a digital twin are for a specific product using a specific processing route. The idea is to eliminate uncertainties in the material models using data collected specifically for the product and its processing route. The model can then be used for in-process quality control or design of similar but new products. This talk presents an overview of recent developments in digital twin and its potential applications in ceramic processing. Firstly new developments in material modelling that underpin the concept of digital twin are reviewed. These include (a) the framework of data driven computational mechanics, (b) dynamic Bayesian network, (c) model order reduction and (d) deep machine learning. Secondly existing material models for ceramic processing are reviewed in the context of digital twin. These include constitutive laws for powder compaction and sintering, discrete element models for sintering and the variational framework for finite element modelling of powder compaction and sintering. Finally conceptional demonstrations are presented to show how a digital twin can be developed for ceramic processing including unconventional processes.

Keywords: Digital twin, Data driven modelling, Constitutive laws

ABS 955

INDUSTRIAL VIEW ON SINTERING TECHNOLOGIES OF THE FUTURE

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Current advanced or technical ceramics are generally processed as powders and consolidated to a dense, homogeneous body through high temperature conventional sintering methods in conventional gas or electrically heated kilns. Typical sintering techniques include pressure-less and pressure-assisted techniques (e.g. hot pressing, hot isostatic pressing (HIP)). The high temperatures involves in sintering ceramics compared to the processing of other materials, and the often extended durations of thermal treatment, mean that ceramic sintering is both energy and time intensive with a detrimental impact onto production economics. A wide range of so called non-conventional sintering techniques have been developed which can help address some of the constraints of conventional sintering, including techniques such as microwave assisted, spark plasma, field assisted and, more recently, the concept of 'cold' sintering. All offer some attractive benefits and as such have received attention from both the scientific and industrial communities. However, despite considerable efforts and advances, there are few instances of a transition into industrial application at scale. This presentation will provide a review of the various non-conventional sintering techniques, looking at their advantages and disadvantages from the perspective of an industrial user, and give comment to the efforts still seen as necessary for further uptake.

Keywords: Sintering

ABS 943

COLD SINTERING OF ELECTROCERAMIC MATERIALS, DEVICES AND NOVEL NANOCOMPOSITES

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Cold Sintering involves a transient phase that permits the densification of particulate materials at low temperatures 300 oC and below. Using this approach, many ceramic and composite materials have been driven to high densities at temperatures far below the melting point under a uniaxial pressure. Densification stages and kinetic scaling laws follow two distinct stages namely particle compaction and dissolution-precipitation processes, respectively. The grain growth process is consistent with classical behavior, but with a much lower activation energy than in a purely thermally driven process. Despite these initial trends having been identified, there is much to be investigated in the liquid-solid interface and intergranular phase development particularly in complex chemistries, and incongruent dissolution processes.

Empowered by sintering at such low temperature offers so many new opportunities, that are also attractive to sustainable production processes. It permits the integration of metastable materials that would typically decompose at high temperatures. So cold sinter enables a platform for better unification of material science. Now ceramics, metal and polymers can be processed under a common platform in one step processes. With controlling the forming process new nanocomposites can be fabricated. Polymers, gels and nanoparticulates can be dispersed, interconnected and sintered in the grain boundaries of a ceramic matrix phase. With the ability to sinter metal phases, multilayer devices can be co-sintered with electrodes made from metals such as Al, Ag, Fe and Cu. With appropriate binder selection, polypropylene carbonate and its de-binding at 130 oC we can remove organic binders and leave metals and other more stable polymers within the layers that then can be co-sintered under the cold sintering process and form unique combinations of materials in multilayers. This then could lead to new devices and devices that can impact important products that are required for a more sustainable economy. Recent, life cycle analysis points to advantages of cold sintering in this regard, however, major advances are required to transition from a batch based process to a continuous production process.

In this talk we will cover some of the fundamental understanding of the cold sintering process. We will also give a number of important electroceramic examples that have been successfully densified that impacts Li-batteries, microwave materials, ferroelectric materials including nanosized $BaTiO_3$ sintered at 300 oC, and semiconductor materials.

Despite the rapid and exciting demonstrations, we will also reflect on future opportunities.

Keywords: cold sintering, electronic properties, microstructure

ABS 953

FLASH SINTERING OF SILICON CARBIDE

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In flash sintering, an electric current is passed through a powder compact during densification. Sintering can be achieved in significantly shorter times than in conventional sintering and with lower furnace temperatures. Most work on flash sintering so far has been on oxides, but the possibility of rapid sintering using lower furnace temperatures would be particularly advantageous if it could also be achieved in non-oxide ceramics such as SiC. This presentation describes progress in achieving the flash sintering of SiC. Various phenomena associated with the rapid heating of the specimen to high temperature and application of high electric fields are found to complicate the process. These include the tendency for plasma formation external to the specimen and reactions producing significant gas evolution. Methods of controlling these are discussed and the effects of the main process variables (e.g. current density, power profile, sintering aids, specimen geometry, sintering time, atmosphere) on sintered density and microstructure are reported. By optimising the conditions, it is shown that high sintered densities can be produced in a few minutes with a furnace temperature of ~1100 °C.

Keywords: flash sintering, silicon carbide, liquid phase sintering

S02

HT PROCESSES AND ADVANCED SINTERING

ORAL PRESENTATIONS

XVI ECeRS CONFERENCE - Abstract Book

ABS 831

ANISOTROPIC SINTERING FOR C-AXIS PARTICLE-ORIENTATED $(Sr,Ca)_2NaNb_5O_{15}$ CERAMICS

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Crystal orientation of functional polycrystalline ceramics is a useful method to improve their properties. Recent works applied the colloidal processing in a high magnetic field to fabricate particle-oriented ceramics. After shaping under the magnetic field, the textured microstructure results from the sintering step.

The objective of this study is to examine the anisotropic sintering behavior of particle-oriented ceramics from initial to final sintering stages, and the associated development of oriented (micro-)structure at various sintering temperatures

As a model, (Sr, Ca)2NaNb5O15 (SCNN) which crystal is tungsten bronze structure was used. SCNN shows a multi-functional property, and candidate of lead-free functional material. In the forming, c-axis is oriented to rotational axis of a rotating magnetic field, since the diamagnetic susceptibility along c-axis is the largest. The anisotropic sintering behavior for each direction, that is parallel and perpendicular to magnetic field, was measured by shadow view technique during sintering. The structure within the particle packing and sintered ceramics were evaluated by powder x-ray diffraction pattern, scanning electron microscopy and electron back scattered diffraction pattern studies.

For oriented sample prepared in magnetic field, the shrinkage and grain growth along the c-axis were higher than those along the a-axis. The anisotropic microstructure development was clearly associated with anisotropic sintering shrinkage. The development of oriented microstructure was caused by the grain growth of oriented particles with taking in random grains. Finally, the highly grain-oriented SCNN ceramics with densified microstructure was obtained via anisotropic sintering. These results clearly show the potential to develop well-defined textured microstructure during sintering by designing and controlling the particle packing structure in a powder compact.

Keywords: particle orientation, anisotropic sintering, microstructure development

ABS 806

INVESTIGATION OF ELECTROCHEMICAL, OPTICAL AND THERMAL EFFECTS DURING FLASH SINTERING OF 8YSZ

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This presentation reports the electrochemical, optical and thermal effects occurring during flash sintering of 8 mol % yttria-stabilized zirconia (8YSZ). In-situ observations of polycrystalline and single crystal specimens revealed electrochemical blackening/darkening during an incubation period prior to flash sintering. The phenomenon is induced by cathodic partial reduction under DC fields. When using a low frequency AC field (0.1–10 Hz) the blackening is reversible, following the imposed polarity switching. Thermal imaging combined with sample colour changes and electrical conductivity mapping give a complete picture of the multi-physical phenomena occurring during each stage of the flash sintering event. The partial reduction at the cathode causes a modification of the electrical properties in the sample and the blackened regions, which are close to the cathode, are more conductive than the remainder of the sample. The asymmetrical nature of the electrochemical reactions follows the field polarity and causes an asymmetry in the temperature between the anode and cathode, with the positive electrode tending to overheat. It is also observed that the phenomena are influenced by the quality of the electrical contacts and by the atmosphere used.

Keywords: Flash sintering, Electrochemicsty, Defects

ABS 745

KINETICS OF LIQUID-ASSISTED DENSIFICATION DURING FLASH SINTERING OF CERAMIC PARTICLES

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Flash sintering is a recent advancement in the electric field assisted sintering techniques, by which the sintering and densification of the nanoparticle compact take place within a few seconds. High electric field and low current density applied to the green particle compact at isothermal condition. The ultrafast sintering is related to thermal runaway at the flash event, which in turn caused by Joule heating. Nevertheless, the atomistic mechanisms active during the rapid densification are still under scholarly debate, whether solid state or liquid-assisted. Recently we showed that the rapid densification can proceed by capillary forces, induced via a liquid-layer formed at the particle contacts. Therefore, formation of a transient liquid-layer, which induces particle rearrangement and is followed by epitaxial crystallization, is energetically preferred. In the present talk the kinetics of wetting and melt spreading from the nanoparticle contacts during flash sintering of ceramic nanoparticles were analyzed. Analysis of the homologous wetting and spreading from the particle contacts revealed wetting velocities of ~ 0.3 micrometer per second and ~ 1 meter per second, induced by the electric field and the capillary forces, respectively. The ultrafast densification kinetics by particle rearrangement is consistent with the theoretical expectations.

Keywords: Flash sintering, Liquid-assisted sintering, Ceramics

ABS 723

EFFECTS OF SINTERING ADDITIVES ON DENSIFICATION MECHANISM OF ALUMINIUM NITRIDE. CORRELATIONS BETWEEN MICROSTRUCTURE AND ELECTRIC PROPERTIES OF FULL DENSE SPECIMENS

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Aluminium nitride ceramics (AlN) have been widely studied for their promising integration in advanced electronic devices thanks to their good dielectric and thermal properties. Aluminium nitride appears to be very difficult to fully densify without sintering aids. However, final properties of AlN ceramics are very sensitive to these aids.

The main objective of this work was to study and to well understand the role of sintering additives like yttria ($Y2O3$) and calcium aluminate ($CaAl2O4$) on the AlN densification mechanism. Finally, the electrical behaviour of the so doped HP-obtained AlN specimens was studied regarding their microstructural features.

Samples of AlN with different amount of additives were sintered by Hot-Pressing in a $N2$ atmosphere to obtain dense materials. The formation of secondary phases was followed by XRD analysis and microstructures were observed by SEM and HR-TEM. In a second time, dilatometry tests under isothermal conditions were performed in order to elucidate densification mechanisms. Furthermore, interrupted sintering cycle was conducted by the use of a quenching system to evidence the mechanisms of phase formation.

Finally, electric characterisations were carried out by leakage current measurement. These latter were relevant to determine the influence of the additive amount on the conductivity variation in a range of temperature [RT – 250°C] and at different voltage [-2kV – 2kV].

An optimum amount of 3wt.% whatever the sintering aid was determined to obtain a fully densified ceramic. Thermal analysis reveals the apparition of low viscous phases at about 1400 – 1500°C, generated at the first stages of the sintering process promoting the densification. These phases were generated by the reaction between the native alumina and the additives ($Y2O3$ and $CaAl2O4$). The so-formed secondary phases, identified as YAM ($Y4Al2O9$), YAP ($YAlO3$) and YAG ($Y3Al5O12$) in the AlN – $Y2O3$ system, were located at the grain boundaries. In the AlN – $CaAl2O4$ system, $CaAl2O4$ and $CaAl4O7$ were so-identified. From these investigations, the chemical composition of these secondary phases evolved to an alumina richer system with an increase of the sintering temperature.

The conduction limit was determined by electrical measurement. In both systems, the increase of additive content leads to a raise of the conduction threshold voltage. The activation temperature of this threshold was shifted from 100°C to 250°C. The conduction mechanism is so clearly influenced by the presence of secondary phases formed during the complete densification.

The formation mechanism during the sintering of AlN with $Y2O3$ and $CaAl2O4$ were evidenced. During the sintering and according the amount of additives, different phases are formed. These secondary phases clearly have an influence on the electrical properties of AlN.

Keywords: Aluminium nitride, Hot-Pressing, Densification

ABS 669

SPS SYNTHESIS OF DENSE AND TEXTURED Ti3AlC2 AND Ti2AlN MAX PHASES COMPACTS – INFLUENCE OF THE APPLIED THERMOMECHANICAL CYCLE ON THE PHASE PURITY AND ANISOTROPY OF THE RESULTING PRODUCTS

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Ternary layered compounds of transition metal carbides and nitrides, commonly known as MAX phase materials with the general formula of Mn+1AXn (M being an early transition metal, A being a group IIIA or IVA element, X being either C or N, and n=1-3) offer a unique combination of metal and ceramic properties. In the present work, high purity Ti3AlC2 and Ti2AlN dense compacts were synthetized by spark plasma sintering (SPS) from respectively TiC/Al/Ti and TiN/Al/Ti powder mixtures under varying sintering conditions.

The effect of the initial molar composition of the powder mixtures, and of the sintering parameters – namely heating rate, dwell temperature, dwell time and applied pressure – on the resulting phase purity and degree of preferential crystallographic orientation of the investigated MAX phases has been assessed through X–Ray Diffraction coupled with Rietveld analysis and microstructural characterization by FIB-SEM-EBSD analysis.

High purity (i.e. > 95%) dense Ti3AlC2 compacts have been obtained after 15 min at 1325 °C under 15 MPa. In the case of Ti2AlN, 5 min at 1400 °C under 30 MPa led to similar level of purity. In both cases, the degree of preferential crystallographic orientation remained moderate at the end of the ‘conventional’ SPS sintering cycle resulting in isotropic physical and mechanical properties (e.g. fracture toughness values of around 7 MPa.m^0,5 were obtained on Ti3AlC2 irrespective of the orientation with respect to the SPS pressing direction).

A clear improvement was obtained through SPS sinter-forging experiments, starting either from fully dense and pure products, or from partially reacted and pre-sintered compacts. After high temperature deformation the resulting microstructure was characterized by a clear alignment of the c-axis of the Ti3AlC2 and Ti2AlN with the compression direction. The effect of this resulting marked anisotropy of the products on their respective mechanical and physical properties has been assessed.

Acknowledgement
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Keywords: MAX phases; Sinter-forging

ABS 623

MICROWAVE SINTERING OF 3D PRINTED CONE-SHAPE CERAMICS: EXPERIMENT AND SIMULATION SYNERGY

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Objectives This paper aims at better understanding and controlling microwave sintering of complex-shape zirconia parts by coupling experiments and numerical simulations.

Materials & Methods Cone-shape ceramics were printed by the process called Robocasting: a ceramic paste is
extruded from a nozzle which is moved across a platform.
Hollow cones with various wall thicknesses, tip angles and heights have been printed from nano-sized yttrium-doped zirconia powder loaded paste. After printing, cones were dried and then submitted to a thermal cycle in order to debind and pre-sinter them, in a conventional furnace.
Sintering was finally performed up to 1500°C in a 2.45 GHz microwave single-mode furnace. The temperature regulation was ensured by controlling the cavity length. Two heating methods were tested: direct microwave heating and susceptor-assisted heating. The temperature was measured with a thermal camera.
The cones were characterized by X-ray microtomography at each processing step (dried, pre-sintered and sintered) with a 6 µm voxel size. The microstructure of the sintered ceramics was observed by SEM.
Finite element simulation of microwave sintering, including electromagnetic and thermal coupling, was carried out with COMSOL Multiphysics R 5.3 software.

Results When the cones were simply laid on their base at the bottom of the insulating box, plasma was observed in the cavity at high temperature. Numerical simulation suggested that this plasma resulted from electrical field gradients in the cavity, especially around the cone tip, due to both this geometrical singularity and zirconia dielectric properties.
In the other hand, when cones were sintered upside-down with the tip drilled into a refractory brick, sintering occurred without any plasma formation. The simulation showed that the support played an electromagnetic buffer role due to its intermediate dielectric properties compared to zirconia and air. However, the geometrical and dielectric ceramic features make heating heterogeneous.
A silicon carbide (SiC) susceptor, partly surrounding the cone, has also been used. This resulted in an hybrid heating with more homogeneous electric field and temperature distributions.

Conclusion
Coupling experimental data and numerical simulations allowed a better understanding of complex-shape sample microwave heating.
Even if it has been possible to complete a direct heating experiment, the use of a SiC susceptor has been favored in order to have a homogeneous heating.

Keywords: Micro-wave Sintering,3D Printing, Finite Element Simulation

ABS 610

UNCONVENTIONAL LOW TEMPERATURE SINTERING PROCESS OF CERAMICS AND MULTIMATERIALS: THE HYDROTHERMAL SINTERING

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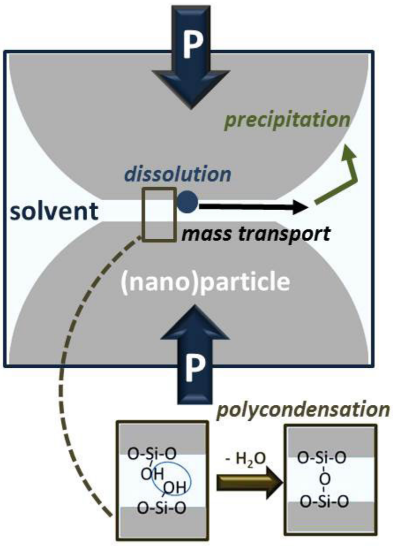
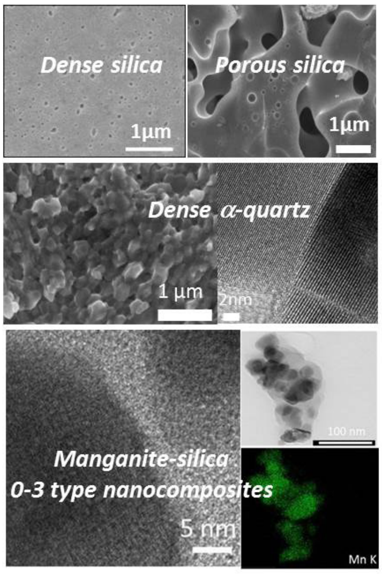
The development of new high performance advanced materials faces the challenge of implementing low temperature densification processes to overcome current technological limitations. Therefore, the impressive performances of processes such as Cold Sintering Process (CSP), Water-assisted Flash Sintering or FAST/SPS, cool-SPS create a tremendous excitement in the ceramists' community. In this context, the hydrothermal sintering (HS), inspired by the natural processes of geological and biological mineralization, has recently emerged as a major opportunity to develop new and/or optimized materials that respond to today's scientific, technological and related socio-economic issues.Both HS and CSP are based on dissolution-precipitation mechanism induced by a pressure solution creep as a driving force for the densification. However, they differ from each other due to the balance between thermodynamics and kinetics that strongly influences the predominance of the involved elementary steps. In the thermodynamically controlled HS, the operating temperature range (<450°C) is not suitable for appreciable bulk diffusion but is sufficient to enhance strong reactivity at the interfaces due to hydrothermal conditions. These specific conditions also represent a powerful lever to tune the nature of the precipitated phase.

The objective here is to present opinions and propose future outlook for hydrothermal sintering based on recent advances (1). The general background and history of the process will be first highlighted. The experimental apparatus and its specific technological design evolution will be described. All the potentialities of hydrothermal sintering will be presented mainly from the results obtained on silica used as a common theme to study the sintering of amorphous (silica) or metastable (α-quartz) materials, to fabricate 0-3 type functional nanocomposites (manganite–silica). A description of the current understanding of chemical and mechanical-chemical mechanisms necessary for densification will be proposed. Finally, opportunities and challenges to expand the method more generically to other systems will be discussed. Some interesting results on other materials will be described.

(1) G. Goglio et al., View point on hydrothermal sintering : main features, today's recent advances and tomorrow's promises, Scripta Materialia 158 (2019) 146

Keywords: Hydrothermal sintering, low temperature sintering, water assisted sintering





ABS 812

SURFACE SEGREGATION OF Li_2O DURING FAST-FIRE SINTERING OF MAGNESIUM SPINEL NANOPOWDERS PREPARED BY PRECIPITATION IN ETHANOL

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Nanomaterials science has shown a growth potential to use small particles with tunable properties to unique properties when compared to micro and macro scales materials, also known as bulk materials. The magnesium aluminate, or spinel (MgAl2O4), when sintered under specific temperature and pressure conditions, becomes mechanically resistant and transparent to certain wavelengths between ultraviolet and infrared. Despite its military and aerospace applications, spinel production with these properties may be costly, because of the exceptionally high pressures needed in the Spark Plasma Sintering (SPS) process in order to densify and keep the grain size into the nano domain. A well succeeded strategy to produce a resistant and transparent spinel is to synthesize nanoparticles doped with Li+ ions, which has been shown to be effective in promoting spinel densification. During this work, lithium doped nano-sized magnesium aluminate spinel was prepared by precipitation in ethanol and fast fired for different times. The material was chemically and physically characterized to evaluate how the kinetics of the dopant segregation on the nanoparticles surface and grain boundaries, two high energy regions that exists in great number in polycrystalline nanomaterials, may influence the decreasing of interfaces energies, contributing to the densification process and nanostability control.

Keywords: Magnesium aluminate spinel, Surface segregation, Lithium doping

ABS 562

DE-DENSIFICATION MECHANISMS OF OXIDES

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In conventional sintering, the final stage usually involves the closure of open porosity and the elimination of these isolated pores to achieve full densification. In some cases, however, swelling can occur to result in the destruction of the ceramic. Such de-densification phenomena (or de-sintering) have been observed in many materials such as ZnO, Fe2O3, superconductors, some carbides and nitrides, nuclear fuels, ITO, (LaSr)FeO3 and BaTiO3 ceramics.
Understanding the mechanisms involved in such damaging behavior is therefore paramount for ceramists, with this subject having been investigated since the 1980s. One type of mechanism is related to the microstructural effects during sintering. The second type of swelling mechanism corresponds to chemical reactions leading to gas formation and eventually to gas entrapment in the pores. This is the case when ZnO is sintered, due to oxide evaporation. The sintering and swelling of BaTiO3 has also been largely studied and discussed, in relation to the decomposition of residual BaCO3. The role of additives should also be taken into account in de-densification.
All these results highlight the existence a range of mechanisms, but the formation of gas during sintering is still the main phenomenon, particularly during the final step of sintering. The possible change in oxidation state during the sintering also appears to be another key parameter, especially for oxides. Therefore, we propose in this presentation to focus our study on a system in which de-densification can occur. We chose an yttria-doped cerium oxide, sintered under reducing conditions. This ceramic has been largely studied and there is a great deal of data available on its thermodynamics and sintering behaviors. Cerium presents two oxidation states and either Ce4+ or Ce3+ can be obtained, depending on the sintering atmosphere. The role of carbon, which is almost always present as a residue of chemical synthesis, is another parameter that we investigated. We also focused on controlling the oxygen partial pressure during sintering, as well as on analyzing the released gases in obtain new insights into the swelling phenomenon. Finally, the experimental de-densification behaviour of the studied oxide (containing or not carbon) has been related to the thermodynamic behaviour of the corresponding system. It also shows the interest of a thermodynamic approach to predict chemical evolution of the oxide that could induce effects on the sintering, such as de-densification.

Keywords: De-densification, Sintering kinetics, Thermodynamics

ABS 527

SYNTHESIS AND STABILITY OF INVERSE MULLITE AND ALUMINA OPALS

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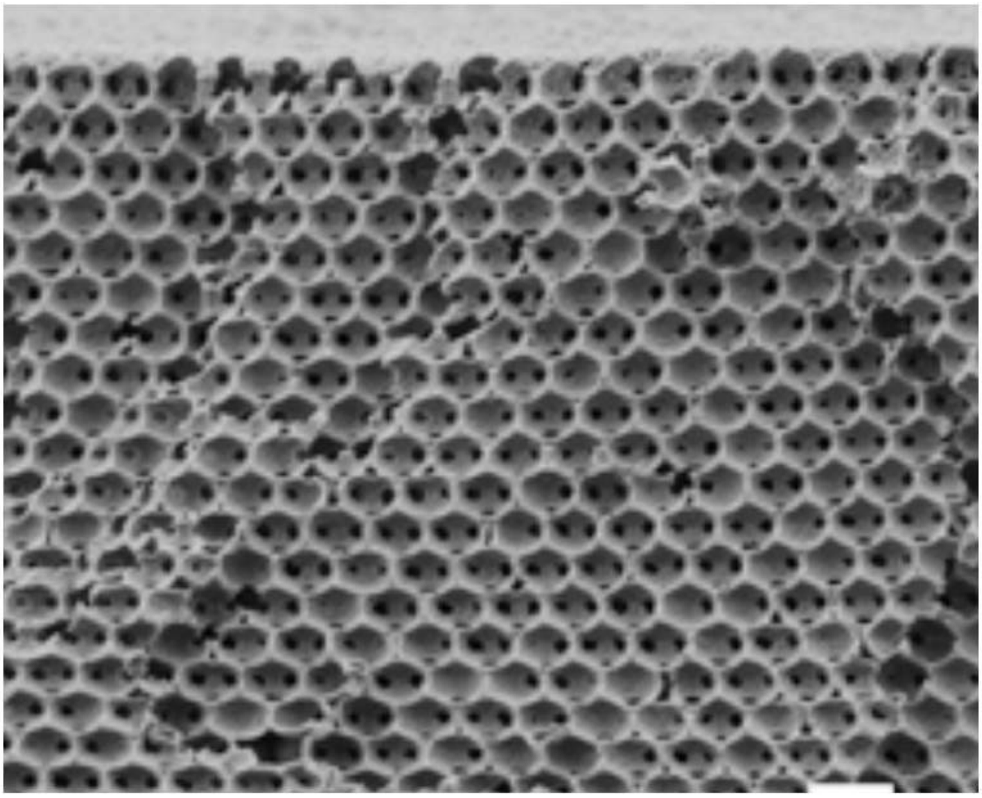
Highly reflective coatings can be created using ordered pores in matrices with high refractive index, e.g. ‘inverse opals’ obtained by inversion of the colloidal crystals offering thereby pronounced photonic bandgaps. For reflecting radiation energy, structures with pores size around the µm range are interesting as they can be considered as candidates for thermal barrier coatings or selective emitter in thermophotovoltaics. At high temperature, however, these structures can exhibit significant undesired microstructural changes (due to phase changes, grain growth, sintering, etc.) that result in a loss of the desired photonic properties.

At present, we focus on Al2O3 and Mullite inverse opals prepared from templates by vertically self-assembled PS monospheres, ALD infiltration and subsequent calcination. In the presentation we will report the synthesis and resultant properties. Particular emphasis will be given to structural changes during heat treatments based on observations from SEM/TEM, X-ray ptychography, nanotomography using synchroton radiation as well as DEM modeling. These confirm that by respective tailoring alumina and mullite thin films with ordered porosity can even serve up to temperatures as high as 1400°C. In addition to Al2O3 and Mullite, also TiO2 inverse opals have been investigated showing a yet unknown stability of the Anatas phase at high temperatures.

Keywords: Inverse photonic crystal, structural stability at high T,3-DOM



Inverse Mullite Opal annealed for 10h at 1000°C and 4h at 1400°C

ABS 518

MIXED MECHANISM PRINCIPLE OF MICROSTRUCTURAL EVOLUTION AND REPETITIVE GRAIN GROWTH IN MATERIALS

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Our investigations on boundary migration and grain growth in the 2000s suggested that the boundary migration is a result of serial processes of diffusion (jumping across the boundary) and interface reaction (detachment and attachment) of atoms. For systems with rough (atomically disordered) boundaries, the migration of the boundary is governed solely by the atom diffusion and its rate is linearly proportional to its driving force. On the other hand, for systems with faceted (atomically ordered), even partially, boundaries, the migration is governed either by the interface reaction or the diffusion of atoms for the driving forces smaller or larger than a critical value. Based on this understanding, we developed the mixed mechanism principle of microstructural evolution. Various types of grain growth behavior were predicted for different relative values of the critical driving force and the driving force for the growth of the largest grain (the maximum driving force in the sample).

Experimental observations on grain growth behavior in many different systems, not only ceramics but metals, have shown the validity of the microstructural evolution principle. The principle can also well explain the recently observed repetitive grain growth behavior, where the behavior changed repeatedly from stagnant to abnormal with respect to sintering time or temperature. In this presentation, we will show the generality of the microstructural evolution principle by presenting some critical experimental results, including the newly observed repetitive grain growth behavior in Ni and BaTiO3.

Keywords: grain growth, mechanism, principle

ABS 506

EFFECT OF CRYSTAL SYSTEM OF ZrO_2 ON MECHANICAL PROPERTIES, THERMAL PROPERTIES, AND SINTERING KINETICS OF Al_2O_3–ZrO_2 COMPOSITES SYNTHESIZED BY MICROWAVE HYBRID SINTERING

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Zirconia (ZrO2) additions in alumina matrix have been found to significantly increase the mechanical properties of alumina (Al2O3). Generally, Al2O3–ZrO2 composites are fabricated by conventional sintering processes. However, these sintering processes consume high energy and long processing times. Microwave hybrid sintering has previously been proclaimed as a solution. But limited research has been executed on the effect of crystal system of ZrO2 on microwave hybrid sintering of Al2O3–ZrO2 composites.

In this research work, microwave hybrid sintering was opted for synthesis of alumina–zirconia composites. Cubic zirconia (c-ZrO2) and tetragonal zirconia (t-ZrO2), 5 wt% each, were used as two different additions in α-alumina matrix. The objective was to scrutinize the effect of two different structural types of zirconia on microwave hybrid sintering of Al2O3–ZrO2 composites. Silicon carbide (SiC) was used as a susceptor material. Mechanical properties including hardness and fracture toughness were investigated. Thermal conductivity was also examined. Addition of cubic zirconia and tetragonal zirconia in alumina showed different mechanisms and results. Al2O3–t-ZrO2 composite showed the highest fracture toughness with a value of 3.67 MPa m0.5, followed by Al2O3–c-ZrO2 composite with a value of 2.75 MPa m0.5, and pure Al2O3 showed the lowest value of 2.58 MPa m0.5. Pure Al2O3 showed the highest hardness, followed by Al2O3–t-ZrO2, and then Al2O3–c-ZrO2, with the values of 19.37, 19.27, and 18.24 GPa respectively. Thermal conductivity showed similar trend to the hardness, with the values of 29.98, 26.26, and 24.12 W/mK for pure Al2O3, Al2O3–t-ZrO2, and Al2O3–c-ZrO2 respectively. These mechanisms were well illuminated by the microstructural analysis which is discussed in detail. Dilatometric analysis was also performed for measurement of activation energy of second stage sintering for pure Al2O3, t-ZrO2 added Al2O3, and c-ZrO2 added Al2O3, which is also discussed in detail.

Keywords: Microwave hybrid sintering, Mechanical properties, Sintering kinetics

ABS 494

INFLUENCE OF HYBRID HEATING AND TOOLING ON THE FIELD ASSISTED SINTERING OF LARGE SCALE OXIDE CERAMICS

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Over the past decades field assisted sintering technology/spark plasma sintering (FAST/SPS) has proven its versatility and potential regarding the densification of diverse material systems like metals, ceramics and composites. The advantages which derive from direct pulsed current heating and applied pressure are high heating rates, rapid densification and decreased sintering temperatures. This enables decreased cycle times and allows the processing of materials that are difficult to densify conventionally. Despite various advantages, industrial applications are still rather limited due to problems which emerge during the up-scaling of the process. Especially the formation of radial thermal gradients is critical for manufacturing reproducible and homogeneous components from electrically non-conducting ceramics.

The present study investigates the formation of thermal gradients during the field assisted sintering (FAST/SPS) of large scale (Ø = 100 mm) yttrium oxide (Y2O3) samples through the coupling of microstructural investigations and finite element simulations. The influence of different tool set ups and the implementation of an additional induction coil, which enables hybrid heating, were evaluated.

Finite element modeling is used to calculate the thermal field during the processing of non-conductive Y2O3 powders. The modeling results are correlated with SEM investigations of the microstructural development over the diameter. Additionally Vickers hardness measurements are used to connect the mechanical properties to the average grain size of the microstructure.

Keywords: FAST/SPS, Hybrid heating, Oxide ceramics

ABS 458

FABRICATION OF ZrC / SiC COMPOSITES USING A PRECERAMIC POLYCARBOSILANE AND SPS SINTERING

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For applications such as in space propulsion systems, re-entry vehicles or cladding materials, ceramics operating under severe environmental conditions and mechanical stresses are highly recommended. Among them, zirconium carbide has a high refractoriness and an interesting mechanical strength. However, its low oxidation resistance limits its use in air at high temperatures. The employment of composite materials based on SiC is a promising way to remedy this problem. Indeed, it exhibits a better resistance to oxidation with the formation of a passive oxidation layer of silica, which limits the degradation of the material [1,2]. In order to confer these high-temperature resistance properties, the control of the chemical composition and microstructures of the composites is essential.

To fabricate these ZrC/SiC composites, a so-called «hybrid» route was used. The latter consists of mixing a synthesized ZrC powder with a preceramic polymer as a source of SiC. The mixture obtained was then ceramized/sintered directly by SPS without prior crosslinking steps of the polymer.

A first part of the work consists in controlling the quality of the synthesized ZrC powders in terms of chemical composition and particle size. Indeed, a pure zirconium oxycarbide with a monomodal granular distribution has been obtained by carbothermal reduction of zirconia.

The second part deals with the mixing procedure in order to obtain easily shaped ZrC/polymer systems. In this part, different amounts of the polymer are tested and their influence on the final texture of the mixtures is demonstrated.

The final part focuses on the optimization of the sintering parameters. A dwell time at three different temperatures (600 to 800 °C) has been set up in order to promote the removal of the organic species prior to sintering. Concerning the sintering temperature, it has been optimized by performing interrupted tests at different temperatures to investigate the evolution of the microstructure during sintering. Well homogenous ZrC/SiC composites have been obtained at 1700 °C.

Reference

[1] B. Ma, W. Han, et E. Guo, « Oxidation behavior of ZrC-based composites in static laboratory air up to 1300 °C », Int. J. Refract. Met. Hard Mater., vol. 46, p. 159 to 167, sept. 2014.

[2] D. Pizon, L. Charpentier, R. Lucas, S. Foucaud, A. Maître, et M. Balat-Pichelin, « Oxidation behavior of spark plasma sintered ZrC–SiC composites obtained from the polymer-derived ceramics route », Ceram. Int., vol. 40, no 3, p. 5025 to 5031, avr. 2014.

Keywords: ZrC/SiC composites, Preceramic polymers, SPS sintering

ABS 457

SINTERING OF ALUMINUM NITRIDE NANOPOWDERS SYNTHESIZED BY THERMAL PLASMA AND COMMERCIAL MICROPOWDERS

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The research for new materials with exceptional properties sets the pace for technological development. Non-oxide ceramics are characterized by high refractoriness, good mechanical properties at high temperatures, and high chemical inertness towards molten salts or liquid metals. More specifically, the AlN has the characteristics of an electrical insulator with high thermal conductivity (320 W.m-1.K-1), and a low thermal expansion coefficient (4x10-6 K-1), which make this ceramic a material of choice for the realization of substrates in the field of microelectronics or optoelectronics. During the last decade, the research field related to the AlN has focused on the use of nanometric powders, either in electronic applications, structural applications or as sintering aids. In this regard, the objective of this research is to study the sintering of AlN nanopowders synthesized by thermal plasma.

The low sinterability of AlN can be related to the presence of covalent chemical bonds and to high refractoriness of this ceramic. This observation leads the ceramist to consider several solutions to densify AlN: I) sintering under load, II) adding sintering additives and finally, III) to use fine powders that are at least submicron or even nanometric.

Taking into account this latest solution, high-purity AlN nano-powders were synthesized by using a 200kW non-transferred arc plasma, conducted in one-chamber thermal plasma reactor. The experimental assembly incorporated: high temperature gradient between the crucible and reactor´s wall, and high super-saturation of the system by nitrogen and carbon. Nitrogen was the only gas, used as the reagent and plasmogenic gas. Aluminum discs of Al 1100 were used as precursor material. Thermodynamic modelling was conducted in order to achieve the best conditions for AlN formation. The synthesized AlN particles, appears as agglomerates, with diameter between 130 and 180 nanometers, constituted by particles of 10 to 80 nanometers.

It is proposed to carry out a comparative study of the sintering process between these AlN nano-powders obtained by plasma, commercial AlN micro-powders and a composite mixture micro-nano powder, by exploiting its physicochemical properties. The addition of nano-powders, can decline the sintering temperature and promote better compaction of the green bodies compared to that observed by using micro-powders, thanks to a significant increase in the specific surface area of the system. In addition, the use of conventional sintering, or HP or less conventional SPS, must allow control densification and granular growth kinetics for obtaining nanostructured objects close to full density with thermomechanical, thermal and electrical exacerbated properties.

Keywords: AlN nano-powders, Sintering HP, SPS, Thermal plasma

ABS 440

HIGH SINTERING EFFICIENCY OF ZrB_2 CERAMICS AT MEDIUM-TEMPERATURE USING POLYMER-DERIVED SiBCN AS A SINTERING AID

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The rapid development of polymer-derived ceramics (PDCs) makes it possible to be the sintering aids for high temperature ceramics. However, the present method of introducing additives by PDCs rout follows the traditional ways of using crystalline power as the sintering aid and the main advantages of PDCs technique are not fully developed. We choose polymer-derived SiBCN as the sintering aid and the liquid polymer precursor is directly introduced into ZrB2 powers without heat pretreatment. The work is focused on the assisting sintering efficiency at medium-temperatures from 1000°C to 1600°C. Liquid polyborosilazane (PBSZ) was mixed into ZrB2 powers at a weight ratio of 16.25 wt%. The mixture was homogenized with n-hexane by ball milling for 1.5 hours. After drying at vacuum atmosphere, the mixture powder was put into a graphite die and pressed into a green sample with a uniaxial pressure of 40 MPa. The densification of the sample was carried out by hot-pressing method in a flowing Ar environment from room temperature to 1600°C for 2 hours with a heating rate of 5°C /min. The pressure of 40 MPa was applied at 800°C and kept until the sintering procedure was completed. The medium-temperature densification curves of ZrB2-SiBCN samples are showed in Fig. 1(a). It is clear that the sintering aid SiBCN has greatly improved the sinterability of ZrB2 ceramics. At 1600°C, the density of the ZrB2-SiBCN samples is increased by 31.6% compared with ZrB2 samples without addition. Especially, the relative density of ZrB2-SiBCN samples increased by 22% in the temperature range of 1300-1400°C. FT-IR and XRD were performed to characterize the chemical structures of pyrolysis product SiBCN and ZrB2-SiBCN samples. As shown in Fig. 1(b-d), the results imply an earlier crystallization process in ZrB2-PBSZ mixture samples compared with pure PBSZ.

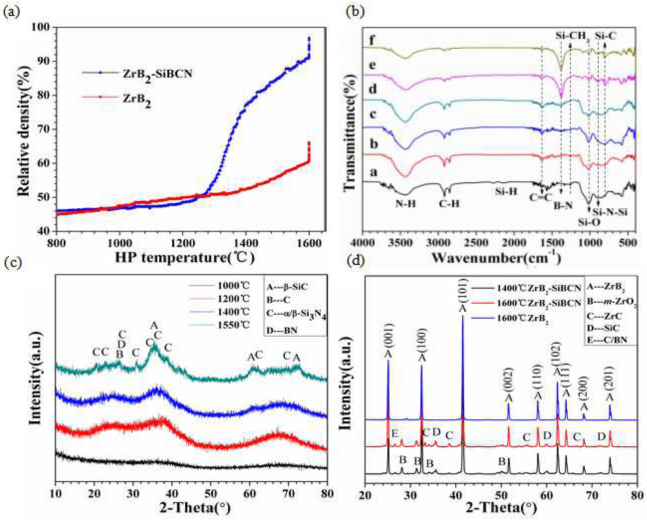

Figure. 1 (a)densification curves of ZrB2 –SiBCN ceramics in comparison with pure ZrB2 ceramics, (b)FT-IR spectra of PBSZ (a 1000°C, b 1200°C, c 1400°C and d 1550°C for PBSZ; e 1400°C and f 1600°C for ZrB2-SiBCN ceramics), (c)XRD patterns of polymer derived SiBCN (d) and the obtained ZrB2 based ceramics.

ZrB2 ceramics using polymer-derived SiBCN as sintering aid show high sintering efficiency at medium-temperature. The oxide impurities on the surface of ZrB2 particles have an influence on the chemical bonding movements and crystallization of the introducing additives. In return, the structural evolution of additions contributes to the microstructure and densification of the composite ceramics.

Keywords: Zirconium compounds, Sintering efficiency, Polymer-derived SiBCN

ABS 413

TRANSPARENT STRUCTURAL AND FUNCTIONAL ALUMINA CERAMICS PREPARED BY PRESSURE-LESS PRESINTERING AND HOT ISOSTATIC PRESSING

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Polycrystalline transparent ceramics are widely used in optical applications in extreme conditions where other optical materials do not meet the requirements for high thermo-mechanical properties and chemical stability (polymers, glass) or are difficult to produce in large and complex shapes (single crystals). Typical applications of these materials include high-temperature windows, transparent armours, missile domes for infrared and combined sensors, infrared emitters, discharge lamp envelopes, optical lenses, high brightness LEDs, optical fibers, laser, dosimeters, etc.

Alumina is one of the most important ceramics for ballistic and optical applications in the visible, near- and mid-infrared wavelengths because of its very high hardness and Young's modulus, chemical stability, thermal conductivity, and competitive strength, fracture toughness, thermal expansion and melting point. Unfortunately, the birefrigency of corundum is a limiting factor for reaching of a high in-line transparency of polycrystalline alumina. Therefore, the processing of this kind of material requires a careful control and an optimisation of all processing steps because of the necessity to reach a fully dense (> 99.99% of theoretical density) and fine-grained (grain size comparable or smaller than incident light wavelength) microstructure. To fulfil these two requirements the Spark Plasma Sintering (SPS) can be used for a powder densification, but with this experimental method the contamination of the sample by carbon cannot be avoided and also the sample shape is limited. In our approach we use colloidal processing of the ceramic powder followed by pressure-less presintering to close the open porosity and by subsequent carbon-free (molybdenum heating and shielding) Hot Isostatic Pressing (HIP). Additionally, an effective doping of the alumina powder helps to inhibit a grain growth and/or to introduce some functionality (luminescence).

In this work, we would like to demonstrate how the control of the powder consolidation (cold plasma activation, proper treatment of dopants), pressure-less presintering of green bodies (presintering heating rate and temperature, or two-step presintering for optimal redistribution of dopants) and HIP conditions (temperature, Argon pressure, dwell time) can influence the microstructure, mechanical (hardness, fracture toughness) and optical (real in-line transmittance, luminescence) properties. Using our advanced approaches we have reached the absolute RIT of 65 % in the case of structural ceramics ($ZrO2$ doping), resp. 57% in the case of luminescent ceramics ($Eu2O3$ doping). Additionally, the rare earth doped alumina exhibited extremely high Vickers hardness (27.6 GPa for Eu doped alumina) and visible (red for Eu-doped alumina, green for Er doped alumina) and near infrared luminescence.

Keywords: transparent alumina, Hot Isostatic Pressing, optical properties

ABS 380

INTERFACE ENERGY DRIVEN DIFFUSION BONDING OF ZIRCONIUM CARBIDE

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Diffusion bonding of ceramics with a metallic interlayer can deliver a variety of joint microstructures including a seamless bond. When applied to ZrC with Ti interlayer [1] such procedure can deliver the seamless joint, depending on the parameters of the process, of which the thickness of the interlayer is particularly relevant. Experiments [1] indicate existence of the critical interlayer thickness, below which the seamless homogeneous joint is obtained, and above which the joint does not homogenize.

We analyze the thermodynamics and kinetics of the diffusion bonding process with metallic interlayer, uncover the driving forces for the diffusion and phase transformations, and, explain the critical thickness of the interlayer. We begin with the sharp interface thermodynamics, then develop the phase field model which predicts the observed behavior.

During the bonding procedure (heating-hold-cooling), Ti first undergoes phase transformation from hcp to bcc. This and the thermal expansion mismatch between Ti and ZrC results in the compressive stresses in Ti. At hold temperature, the key process is the diffusion of carbon from ZrC into Ti, which, when the critical carbon concentration is reached, initiates the phase transformation of bcc Ti (with interstitial C) to B1 structure (TiC) identical to ZrC structure. The binary Zr/Ti diffusion is then driven by entropy and results in a seamless Zr(Ti)C joint.

Analysis of phase diagrams of Zr-C and Ti-C systems and elastic strain energies indicate that the changes bulk free energies resulting from small changes in carbon concentrations oppose the diffusion of carbon. We show that the only component of the total system energy that decreases with carbon transfer from ZrC to Ti is the interface energy. Specifically, the interface energy must depend on the jump in the carbon concentration across the interface, in such a way that a lower concentration jump produces a lower interface energy.

The critical film thickness is then estimated as the ratio of the change in interface energy with the concentration jump to the change in bulk energy density (elastic and/or chemical). The sharp interface model yields an estimate for the critical thickness of 10 microns, while the phase field simulations of the diffusion bonding process with a range of film thicknesses predicts the value of 32 microns, both in good agreement with experimental findings (10-50 microns).

The analysis and methods are applicable to the broad range of transition metal carbides.

[1] Pan, R et al, 2016, Scripta Mater. 112, 42-45.

Keywords: transition metal carbides, interface energy, diffusion bonding

ABS 360

EFFECT OF DC CURRENT ON HIGH TEMPERATURE DEFORMATION OF ZIRCONIA CERAMICS

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Recently, the current effects on the high temperature phenomena have been attracted considerable attention in the field of ceramics processing. Especially, flash sintering phenomena, which was firstly reported by Raj and his colleagues in 2009, has been the subject of many paper of ceramic sintering. This is because the flash event can succeed to lower the sintering temperature of several ceramic powders. On the other hand, Conrad and his colleagues examined the effect of electric fields on the high temperature tensile properties of 3Y-TZP and confirmed that the fields can lower the tensile flow stresses of 3Y-TZP enough to attain superplasticity. The enhanced deformation was explained by suppressed grain growth due to the electric bias effect. However, the mechanism/phenomena of the flash event are still unclear. In order to clarify the effect of electric current on high temperature deformation, therefore, the present study was carried out to examine the tensile behavior of polycrystalline zirconia ceramics under the several temperature and electric field/current conditions.

By applying the DC electric power higher than a critical value Ec, the flash event similar to that of powder sintering occurs even in dense zirconia ceramics. At around 1000 °C, for example, the Ec value is about 100 - 200 mW/mm^3, which is slightly larger than those reported in the powder compacts. For lower than Ec, the applied electric current increases sample temperature depending on the applied value, but does not enhance the rate of deformation. For higher than Ec, on the other hand, the electric current enhances the rate of the deformation to about several times as compared with that of without current conditions. The enhanced deformation cannot be interpreted only by the increment of sample temperatures and is likely to occur by the flash event. After the deformation under the electric current conditions, the tested sample shows slight gray color even under air condition. This suggests that the enhanced deformation would be related to oxygen vacancy formation. In the presentation, we will discuss the detailed current effect obtained at wide range testing conditions.

Keywords: flash sintering, current effect, high temperature deformation

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EFFECTS OF REACTION SINTERING PROCESS ON MECHANICAL PROPERTIES OF B_4C COMPOSITES

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It has been known that very high sintering temperature is necessary to sintered monolithic B4C close to the theoretical density. However, the mechanical properties such as flexural strength as well as fracture toughness of monolithic B4C are not good enough to apply it to various industries, although B4C shows extremely high abrasive wear resistance. In this studies, various B4C based composites such as B4C-TiB2, B4C-TiB2-C, and B4C-TiB2-SiC-C composites were synthesized by in-situ reaction sintering process including hot pressing using various starting materials. The reaction sintering processes were found to be very effective to fabricate B4C composites with high relative density at relatively low temperature. The microstructures of sintered B4C composites were examined by means of X-ray diffraction, SEM, and EDX. The fabricated B4C composites were consisting of 45~90 vol.% B4C, 5~25 vol.% TiB2, 0~20 vol.% SiC and 0~10 vol.% graphite depending on compositions of starting materials and sintering temperature conditions. The newly formed TiB2, SiC and graphite during reaction sintering process were embedded both inside B4C grain and at grain boundary. The mechanical properties of reaction sintered B4C composites were much enhanced compared to those of monolithic B4C. The flexural strength and fracture toughness of reaction sintered B4C composites were 450-700 MPa and 4-12 MPam½, respectively.

Keywords: B4C composite, reaction sintering, mechanical properties

ABS 288

MICROWAVE SINTERING OF NUCLEAR CERAMICS

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Mixed oxides (MOX) made of PuO2 and UO2, in the form of sintered pellets, are used as fuel in nuclear reactors. The sintering step is generally carried out at high temperature (about 1700°C) in an electrical resistance furnace. Therefore, there is a need to optimize manufacturing processes and especially to reduce economic and energetic costs. To this aim, microwave heating has been extensively investigated as an alternative technology for sintering of ceramics. In this process, the ceramic components are directly heated by absorption of the microwaves, leading to substantial savings in processing time and energy. It is known that actinide oxides have high dielectric losses, thus can be heated at high temperatures with microwaves. However, very few studies reported the fabrication of sintered UO2 pellets employing microwave heating. The main issues of these studies are the poor reproducibility and the lack of relevant comparison between conventional and microwave sintering. Therefore, the main aim of this work is to perform an in-depth study of the microwave sintering of nuclear ceramics. The control of the heating cycle and the measurement of sample's shrinkage are of particular importance to highlight possible microwave effects during sintering. For this purpose, a suitable cavity for multimode microwave sintering was designed and fabricated. The cavity was developed to be used in a glovebox (dimensions, handling of the setup) while allowing an optimized heating of the samples. A sintering cell was also designed with the aim of uniformly heating the sample. The cavity and the sintering cell were fabricated and improved thanks to finite element simulations and preliminary tests with a surrogate of UO2. The microwave sintering setup also includes different devices for non-contact measurement methods such as pyrometers for temperature and optical dilatometer for shrinkage measurement of the sample. First sintering tests of UO2 pellets showed the feasibility of microwave sintering with a shorter thermal cycle (lower than 4 hours) and a shorter energy consumption compared to conventional sintering. In situ and non-contact measurements of temperature and shrinkage now allow a relevant comparison of conventional and microwave sintering of MOX samples. It will then be possible to investigate the existence of a possible microwave effect during sintering of MOX and actinide oxides.

Keywords: microwave sintering, uranium dioxide, nuclear fuels

ABS 275

HIGH CONTRAST AND ENDURING LASER MARKING OF ALUMINA

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The identification of ceramic pieces or elements is essential in many applications. Alumina is a ceramic widely employed in many different industries, however the printing of permanent marks or lettering on it is still a complex problem. In this sense, lasers have largely demonstrated their high capacities to mark almost every material including ceramics, but producing dark marks on alumina is still an open challenge.

In this work we present the results of a comprehensive experimental analysis on the process of marking alumina by laser. Five different laser sources were used in this study: two different fiber lasers with very similar emitting wavelengths of 1070 nm and 1075 nm but very different radiant power characteristics. Also, three pulsed diode pumped Nd:YVO4 lasers were employed emitting at near-infrared (1064 nm), visible (532 nm) and ultraviolet (355 nm) respectively. The results obtained with the four lasers were compared, we demonstrate the influence of the surrounding gas and propose an explanation of the physical processes involved. Colorimetric analyses allowed to identify the optimal parameters and conditions to produce everlasting and high contrast marks on alumina. The coloration of alumina by laser marking has been formerly explained based on the generation of oxygen vacancies, which are identified as color centers. Previous analyses on the influence of inert or oxygen atmosphere on the ultraviolet laser marking demonstrated the influence of inert atmosphere. Notwithstanding the conclusions of these works are mainly based on the analyses of oxygen vacancies by XPS, we postulate that this technique can't be employed to assess the concentration of color centers required for alumina coloration, and, moreover, the previously published works are not consistent among them. Alternatively, we present a set of experiments revealing some results which are consistent with our hypothesis.

Keywords: laser marking, alumina, colorimetric analyses

ABS 223

ANISOTROPIC THERMAL CONDUCTION IN HIERARCHICALLY STRUCTURED COMPOSITE USING GRAPHENE-AUGMENTED ALUMINA NANOFIBERS

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Anisotropic thermal conduction was achieved in a spark plasma sintered multi-layered ceramic composite with a thin thermally conductive interlayer reinforced by graphene augmented alumina nanofibers (GAIN). The structures were implemented using solution and filtration system to deposit layers directly into the SPS mold. Presence of electrically and thermally conductive GAIN fibers led to significant grain refinement and together with low temperature (1150 °C) sintering resulted in a nearly translucent structure. Room temperature thermal conductivity measured by a steady state method was 55 W/m.K considering the entire cross section of the sample (~1 cm). This value is an improvement on 30 W/m.K thermal conductivity of a monolithic alumina reference. However, considering the thin (100 µm) cross-section of the conductive hybrid interlayer, the measurement suggests an incredibly high thermal conduction of 2160 W/m.K.

Keywords: Alumina, Graphene, Layered Structure

ABS 216

IMPACT OF MAGNESIA ON SODIUM CONTAMINATION DURING FORMATION OF SPINEL IN ALUMINA – 3D GRAIN SIZE ANALYSIS

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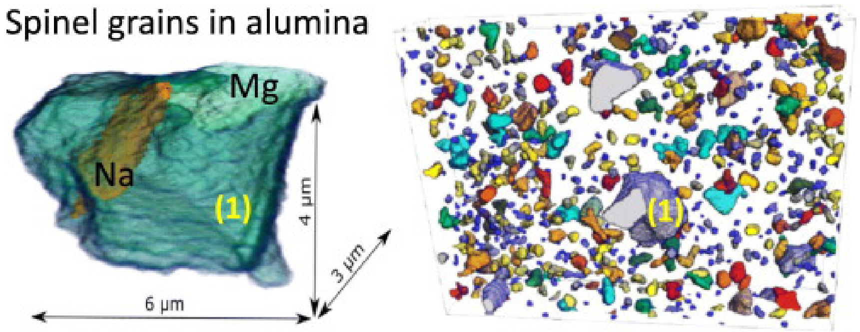
Microstructural study of MgO-doped alumina was done in various conditions, spinel MgAl2O4 phase could be present and it has significant impact on mechanical properties. Overall concentration of the dopant is low, but locally it could reach concentration necessary for the spinel formation. Therefore, two competing processes including MgO are present: the distribution of MgO on alumina grain boundary and formation of new phase – spinel. Globally up to concentration of 0.1 wt. % MgO and alumina forms solid solution, however local conditions (in level of micrometers) can be significantly different. Furthermore, low concentrations of impurities can also have an impact on grain size distribution after sintering.
In this work, the sensitive 3D method of analysis - time-of-flight (TOF) SIMS with horizontal cross-sectioning was used to monitor Mg and Na distribution. As a result, 3D chemical analysis at nanoscale was made to describe spinel crystals formed inside the alumina matrix as well as presence of sodium. The prepared alumina doped with MgO was in the final sintering stage, formation of the spinel phase was confirmed by X-ray diffraction analysis (XRD).
The formation of the spinel we successfully measured in the alumina for different concentration of MgO using 3D TOF-SIMS imaging. Majority of spinel grains have a volume below 1 μm^3, however, also the grains with a volume of tents of μm^3 are presented. Sodium impurities presented in the starting powder were concentrated during sintering nearby or in the spinel grains and its locally concentrated. The impact of this phenomena on grain growth has to be further investigated.


Spinel grains in alumina

R. Holenak, T. Spusta, M. Potocek, D. Salamon, T. Sikola, P. Babor, 3D localization of spinel (MgAl2O4) and sodium contamination in alumina by TOF-SIMS, Materials Characterization 148 (2019) 252-258.

Keywords: MgO-doped alumina,3D grain size, spinel

ABS 211

HIGH-TEMPERATURE REDOX PROCESSES IN $Ce_{0.5}Zr_{0.5}O_{2-x}$ PHASES PRODUCED BY LASER-ASSISTED DIRECTIONAL SOLIDIFICATION

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Rods of Ce0.5Zr0.5O2-x composition were melted and crystallized by laser-assisted directional solidification. The stoichiometry, crystal structure and microstructure of the resulting material were studied by X-ray diffraction, scanning electron microscopy and Raman scattering. The conditions resulting in cation ordered, pyrochlore-like, or cation disordered, fluorite-like phases were determined by varying the sintering and processing atmosphere. The effect of varying other parameters such as the rod diameter and the processing speed was also investigated, as well as phase evolution upon post-processing thermal treatments. The radial spatial distribution of the crystallized phases was interpreted in terms of high-temperature redox reactions and oxygen diffusion through the melt. We conclude that at the high temperatures reached to achieve melting (> 2000 °C) cerium is always reduced, as per the 2Ce4+(melt)+ O2- (melt) < = > 2Ce3+ (melt) + ½O2(g) reaction, but the final reduction degree varies depending on the oxidizing or reducing character of the processing atmosphere. The balance between the oxygen concentration of the starting material and oxygen diffusion toward the surface determines the degree of Ce reduction and thus of cation order in the processed material. Oxygen storage properties were analyzed by TGA and TPR techniques.

Keywords: oxygen storage compounds,CeO2-ZrO2,laser floating zone

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FLASH SINTERING OF LEAD FREE POTASSIUM SODIUM NIOBATE PIEZOELECTRICS

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Either for sustainable production of materials or for improving performance, alternative sintering processes are needed and currently being object of study and development. In this work we have used FLASH to sinter Potassium Sodium Niobate, K0.5Na0.5NbO3 (KNN), a lead-free piezoelectric. FLASH sintering is a Field Assisted Sintering Technique that allows the reduction of both sintering temperature and time. In the case of KNN, FLASH has additionally the potential to overpass the limitations found in conventional sintering, i.e., secondary phase formation and limited final density (< 95 % of relative density) due to alkalis volatilization at high sintering temperature (> 1100 °C) and time (> 2h). Here we show that KNN sintering temperature in air can be reduced to below 900 °C, when a field of 300 V/cm and current limit of 20 mA/mm^2 are used. In this case, densification over 95 % is possible to reach without the appearance of secondary phases. Interestingly, we found that FLASH sintering temperature (TF) can be further reduced, to below 300 °C, when a combination of reductive / water rich atmosphere is used, as can be seen in figure 1. In this case the effect of particle size and applied electric field on the attained density was investigated. Transmission Electron Microscopy (TEM) was used to access FLASH sintered KNN microstructure, specifically in what concerns grain boundaries (GBs) and particle contacts. In parallel, Finite Element Modeling (FEM) was used as a tool to model electric field, current and Joule Heating distribution on the particle surface. Both techniques allowed to conclude that KNN presents amorphized GBs that result from the surface particle melting. The melting induces impurities segregation at the GBs and densification by particle sliding and viscous flow. The dielectric properties of FLASH sintered KNN (at 900 °C, electric field of 300 V/cm and current limit of 20 mA/mm^2), in terms of phase transition, dielectric permittivity and losses, are similar to those of conventionally sintered KNN at 1100 °C for 3h.

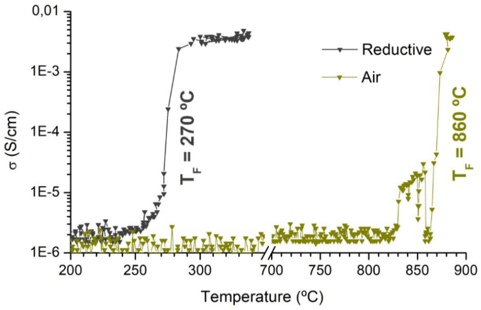

Figure 1 – KNN logarithmic conductivity dependence with temperature, for two different atmospheres: air and reducing. An inset for FLASH temperature is presented for each curve.

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Keywords: FLASH sintering, Lead free piezoelectrics, Advanced sintering

ABS 188

EFFECT OF ELECTRIC CURRENT DURING THE INITIAL SINTERING STAGES OF ZIRCONIA

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The linear shrinkage during isothermal treatment in the early stages of conventional and field-assisted sintering of 8 mol% yttria-stabilized zirconia was analysed. The results reveal that the application of a moderate electric current causes a remarkable acceleration of the self-diffusion kinetics, resulting in enhanced densification.

In addition, when an electric current is applied, two different field-assisted sintering regimes can be identified. The first one, observed at low currents (i.e., 5 mA/mm2), is associated to sintering shrinkage which follows the conventional trend (ε ~ t^(1/3)) although the densification is accelerated. The second regime takes place when larger current are applied (J > 10 mA/mm2) and is described by a different sintering law, ε ~ t^(1/7), this pointing out that the electric current causes the activation of alternative densification mechanisms when it exceeds a certain threshold value.

Keywords: sintering, field-assisted sintering, zirconia

ABS 185

LASER SINTERING OF OXIDE CERAMICS: STATE TRANSFORMATION, REDUCTION, AND MORE EMBEDDED IN THE HETEROGENEOUS STRUCTURE

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Compared with the versatility in sintering of metals, the application of laser on sintering of oxide ceramics is quite limited due to intrinsic features of ceramics and limited understanding in laser-ceramic interaction mechanism, especially for high-energy laser that causes local melting. What will be reported in this presentation is the results of a study into general behaviors of several oxide ceramics melted, rather than sintered, by laser under inert atmosphere. Key factors in determining the related transformation are summarized as basic principles, with further investigation into the evolution in microstructure at multiscale and the corresponding novelty and metastability. It was found that besides acting as a heat source, as commonly thought before, laser does stimulates local melting, which introduces further deep reduction, unique microstructure, and notable increase in structure complexity and total entropy. Such a highly nonequilibrium process could be an alternative approach towards fabrication of traditional oxide ceramics with unconventional functional performance, based on the contribution of those features with novel structure-property relationship.

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Keywords: laser sintering, oxide ceramics, heterogeneity, defects, non-equilibrium

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REACTION SINTERING OF SILICON CARBIDE CERAMICS BY DIRECT LASER HEATING

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Silicon carbide (SiC) is a promising structural material due to its excellent mechanical and thermal properties, and a reaction sintering technique is widely used to obtain SiC parts. However, reaction sintered SiC parts contain a large amount of residual Si metal (5-10 vol.%), and the residual Si causes a degradation of the mechanical properties at a high temperature. Laser heating has been developed as a heating process for ceramics . The laser heating is possible to heat samples rapidly and the process time could be shortened. In this study, the laser heating was applied to the reaction sintering of SiC.
Commercial high purity silicon (Si) and carbon (C) powder were mixed at Si:C=1:1 molar ratio, and pelletized by an uniaxial press at 10 MPa and a subsequent cold isotactic press (CIP) at 245 MPa. A CW Nd:YAG laser (laser power (PL) = 0 ~ 300 W) was defocused and irradiated to the pellet covering the whole surface under Ar atmosphere. The microstructures and Vickers hardness of the irradiated samples were investigated.
Figure 1 shows the scanning electron microscopy (SEM) images of the sample obtained at PL =200 W. The surface was dense, and contains faceted grains. The polished cross-section showed an island structure, where grains of 1-5m in size were dispersed in the matrix. An electron backscatter diffraction (EBSD) pattern of the cross-section is shown. The grains were 3C-SiC and the matrix was silicon. The average Vickers hardness of the sample surface using nano-indentation technique was 2362 HV, which was almost the same as a SiC wafer.

Keywords: Laser direct heating, SiC, Reaction sintering

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SINTERING OF LITHIUM HYDROXIDE DOPED MAGNESIUM ALUMINATE SPINEL

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Magnesium aluminate spinel has been widely used in engineering applications owing to its excellent chemical, thermal, mechanical and optical properties. However, sintering of spinel is difficult. Dense polycrystalline spinel ceramics are usually obtained by sintering at high temperatures, often > 1600°C. High sintering temperatures then result in deterioration of mechanical properties due to extensive growth of spinel grains. The present work is aimed at improvement and study of the process of densification of magnesium aluminate spinel through the addition of a small amount of lithium hydroxide.

Magnesium aluminate spinel powder, ACS> 99.0 %, was mixed with various amounts of lithium hydroxide, 0-1.2 wt%, in distilled water by using an ultrasonic mixer. Afterwards, the mixtures were dried and granulated using a rotary evaporator. Green bodies were produced by uniaxial pressing of dried powder at 70 MPa. Sintering was carried out in a dilatometer at the temperatures up to 1550°C, applying different heating rates. Master sintering curve approach was used to explore the influence of LiOH doping on densification/sintering of spinel ceramics. The reactions between spinel and lithium hydroxide were studied by differential thermal analysis and high-temperature X-ray diffraction. The microstructure of samples was examined using scanning electron microscopy.

The results indicate that highly dense spinel bodies can be obtained by the addition of a minute amount (0.3 wt%) of lithium hydroxide. Doping with LiOH significantly decreases the apparent activation energy of sintering (960 kJ.mol-1 vs 450 kJ.mol-1). Interestingly, the grain size distribution of the 0.3 wt% LiOH doped samples is similar to that of the pure spinel: the addition of minute amounts of LiOH has no significant effect on grain growth. Thermal analysis showed that lithium hydroxide was decomposed to lithium oxide upon heating to 800°C. Lithium oxide dissolved in the spinel structure with the increasing temperature, producing oxygen vacancies. This facilitates oxygen diffusion, thus promoting mass transport in the material. XRD results revealed that lithium aluminate ($LiAlO_2$) was produced as the result of high-temperature reactions between $MgAl_2O_4$ and Li_2O.

Lithium hydroxide can be used with success to decrease the sintering temperature of magnesium aluminate spinel. The addition of a small amount of LiOH (0.3 wt %) promotes densification of spinel ceramics. LiOH facilitates oxygen diffusion and improves densification. Moreover, precipitation of $LiAlO_2$ phase is responsible for the impediment of grain boundary movement and hence, limited grain growth.

Keywords: Magnesium aluminate, Spinel, Sintering

ABS 133

THE EFFECT OF PRESSURE APPLYING REGIME ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NANO-ALUMINA DURING SPARK PLASMA SINTERING

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Abstract—One of the most novel sintering technique, Spark Plasma Sintering (SPS), has been studied over decades. The main feature of SPS is the extremely high heating rate up to 2000 oC /min accompanied with pulsed direct current and applied pressure during sintering. Numbers of researchers have investigated the impact of fast sintering speed and applied pressure in the past twenty years. However, the pressure applying regime doesn't attract much attention. In the present study, four different pressure applying regime from the beginning, 600oC, 900 oC and sintering temperature with one pressureless SPS have been studied during SPS of Nano-Alumina powder at 1100 oC, 1150 oC, 1200 oC and 1300 oC, respectively. The results show that the samples sintered with pressure have high density and hardness than that sintered without pressure. The highest hardness is achieved at 1150 oC, 1200 oC, 1200 oC and 1300 oC when pressure is applied at the beginning, 600 oC, 900 oC and sintering temperature, respectively. The microstructure and grain size of each sample is observed and calculated carefully by a statistical method. That the interaction between pressure and pores leads to different diffusion rate of grain boundary at different temperature stage is considered as the main reason for the differences of the microstructure. In addition, the mass transport and grain growth activation energy during SPS are also discussed and concluded.

Keywords: Spark Plasma Sintering, Pressure applying regime, Microstructure

ABS 127

REAL-TIME AND 3-DIMENSIONAL OBSERVATION OF SINTERING BEHAVIOR OF ALUMINA GREEN BY OPTICAL COHERENCE TOMOGRAPHY

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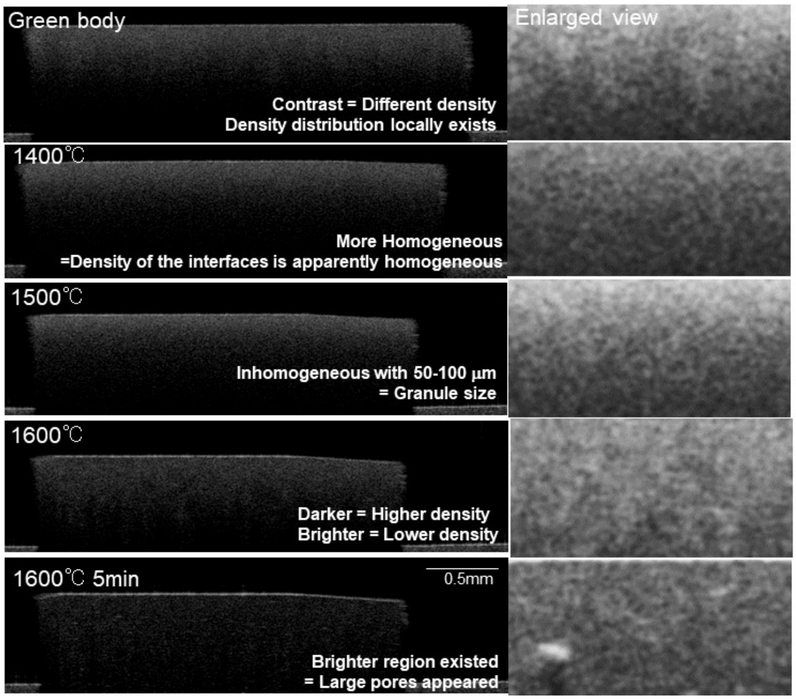
It is well known that bonding of particles, decrease in surface area, and shrinkage of a powder compact occurs dynamically in sintering of ceramics. Although the internal structure of the ceramics have to be controlled to make better ceramcs, evolution of the internal structure during sinterin at high temperatures has not been clarified yet. In this study, real-time and 3-dimensional observation of sintering behavior in a ceramic powder compact was carried out by optical coherence tomography (OCT). Commercially available Al2O3 powder was used as a raw material. After adding the small quantity of MgO and molding the powder mixture by dry pressing, the powder compact was set in the electric furnace. OCT observation was carried out through a glass window from the above of the furnace. The internal structure of the powder compact was clearly observed at high temperatures without the effect of any heat radiation as well as at a room temperature as shown in the figure. It was also found that the powder compact shrunk gradually with heating. The inhomogeneous region existed before firing, but it disappeared in the initial stage of the sintering shrinkage. When the relative density was over 90%, contrast of the sea-island structure appeared because of the difference in the porosity. After the contrast faded out again, the different inhomogeneiety was observed, resulting from the coarsening of the pores. In the case of a green prepared using raw material by adding granules composed of large grain, inhomogenous regions resulting from insufficient densification appeared. The green of layered structure composed of different particle size indicated large deformation and cracking in alumina green during sintering. Consequently, it was shown that OCT is powerful tool to observe directly and 3-dimensionally the appearance and the internal structure of a ceramic powder compact during sintering.

Keywords: Optical Coherence Tomography, Real-time and 3D observation, Internal structure



ABS 126

INTERACTION BETWEEN SiC AND Ti_6Al_4V IN THE SPS – FROM WETTING STUDIES TO JOINING

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A new advanced technique to assess the wetting behaviour of molten metal/ceramic system at very high temperatures was developed using the Spark Plasma Sintering (SPS) apparatus. Such a wetting test simulates the real conditions during the joining of ceramics using a metal interlayer by SPS.

The interaction between the molten Ti6Al4V alloy and the CVD-SiC was thoroughly investigated by the wetting studies conducted in the SPS at various temperatures, heating rates, dwell times and environments. Both, wetting and spreading of the alloy on the SiC surface were significantly improved with the increased heating rate. The SEM analysis showed the extensive reaction between the SiC substrate and the molten alloy, leading to the formation of TiC and different Ti-Si-Al-V-C systems. When the wetting was investigated at 1600°C using a heating rate of 1000°C/min, the formation of reaction products was sufficiently suppressed and very good wetting was observed. The alloy even spread over the entire surface of the SiC cuboid.

However, the pressureless joining in the SPS was not successful even when different heating and cooling rates were applied. After joining, the alloy either delaminated from the SiC surface, or was extremely porous and wavy. On the other hand, after applying a minimum external pressure (at the level of 15 MPa) a sound joint was obtained after joining at 1600°C. An extensive infiltration of the alloy into the CVD-SiC was observed, which helped the joining filler to be well integrated with the matrix. This was the reason of a high bending strength of the joints (~ 220 MPa), reaching the value of the reference unjoined CVD-SiC material. More importantly, the joints showed an excellent strength retention at high temperatures, as the bending strength of the joints measured at 1300°C was still ~ 150 MPa (~ 66% of the initial bending strength).

Acknowledgment

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Keywords: wetting, joining, spark plasma sintering

ABS 120

RAPID MANUFACTURING OF CERAMICS BY COMBINING STEREOLITHOGRAPHY AND MICROWAVE SINTERING

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Stereolithography (SLA) is an additive manufacturing method that permits to make complex-shaped pieces in short time. However, usually, long debinding and sintering steps are required in order to obtain sintered pieces, which is a problem considering the need to keep a fast manufacturing process. Thus, the use of microwave heating to debind and sinter the green pieces seems to be a promising way to achieve a rapid manufacturing of sintered complex-shaped pieces.

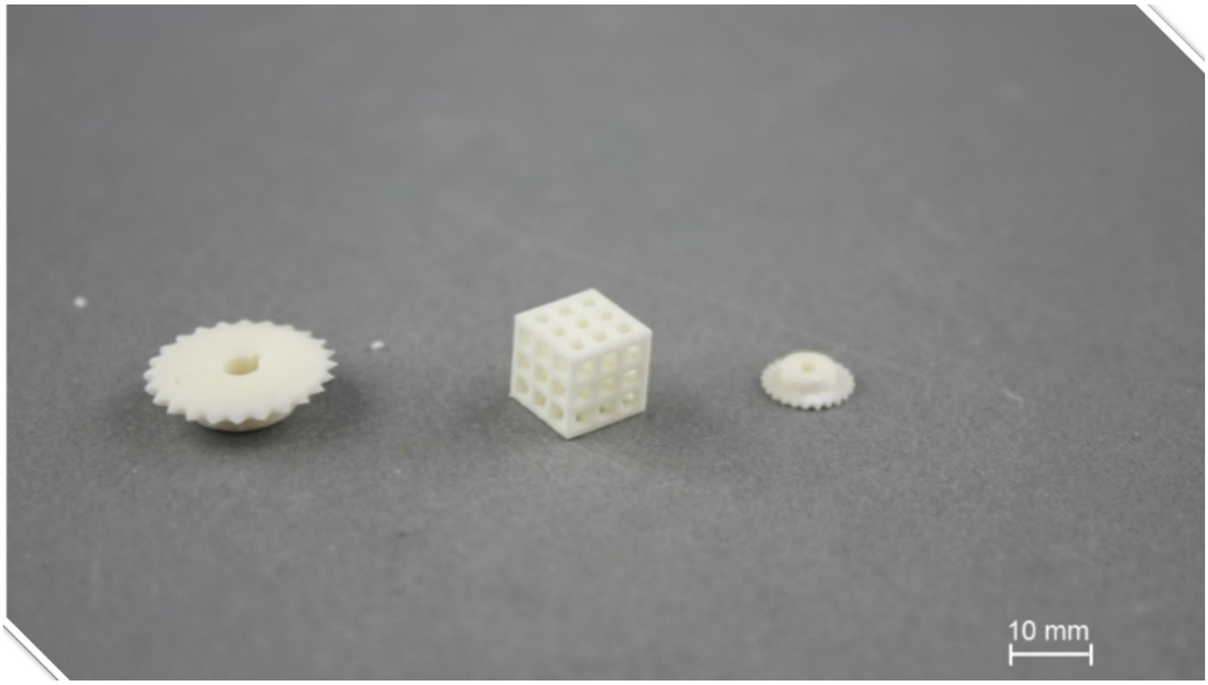
In this study, the ability to manufacture bioceramics (hydroxyapatite and alumina) by combining these two processes is highlighted. Indeed, the use of macroporous complex geometries for bones substitutes is necessary in order to enhance cells colonization.

In the case of hydroxyapatite, after a 40 minutes manufacturing step by SLA, microwave debinding and sintering are carried out in about 60 minutes. To do so, an 80 nm powder is used and a dry matter of 65% in mass is applied to prepare the slurry. A final relative density of 98% is reached for the pieces walls. Moreover, a finer grain size, compared to the one obtained after conventional sintering, leads to higher hardness values.

Concerning alumina, two powders presenting two different gain sizes (1.3 and 0.4 µm) were investigated. The first one is optimal for the SLA manufacturing step, leading to a suitable viscosity value and so to correct shape. However, the sintering temperature is about 1700°C, which is too high for the microwave device and does not permit to reach high relative density values. Thus, a bimodal powder mixture was used to be able to proceed to SLA shaping but also to decrease the sintering temperature. After microwave debinding and sintering a density of about 94% is reached (Figure 1).

Finally, microstructure and mechanical properties of the dense samples were determined and compared to those obtained after conventional manufacturing.

Keywords: Microwave sintering, Additive manufacturing, Alumina



ABS 95

MULTI-PHASE ARMOR PRODUCTION AND CHARACTERIZATION INVOLVING B_4C–SiC–TiC WITH SPS TECHNIQUE

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Boron carbide (B4C) is the most commonly used material for armor applications due to its light and high hardness. However, the high cost is one of the most important obstacles in the front. On the other hand, sintering is very difficult and requires sintering with a hot press (HP) at temperatures around 2200 °C to bring it to the theoretical density. However, the mechanical properties of monolithic B4C are not good enough to be used in industrial applications. _For this reason, numerous studies have been carried out on the production of B4C -containing composite materials by the addition of different compounds such as silicon carbide (SiC) and titanium carbide (TiC). The addition of these compounds improves both the properties and reduces the sintering temperature.

In this study, optimum B4C-SiC-TiC multi-phase ceramic composite compositions were designed and produced by spark plasma technique bearing in mind the hardness – toughness – cost – lightness - performance relationship. In addition, the effect of these carbides was also investigated by adding only TiC or SiC powders into pure boron carbide powder. The addition of SiC did not affect the hardness and toughness, but the addition of TiC resulted in increased toughness in spite of decreased hardness. When microstructure analyzes and x-ray diffraction patterns were evaluated together, residual graphite and SiC were found to exist in pure B4C, and when TiC was added, residual graphite and small amounts of SiC, as well as TiC and B4C, reacted to form titanium diboride (TiB2). When SiC and TiC were added together, hardness decreased whereas fracture toughness increased. Because of the fact that boron carbide is a light material, all the additives added increase the weight, while the costs were reduced because all the additives are cheaper than B4C.

Keywords: B4C,SiC,SPS

ABS 92

SINTERING BY MICROWAVE HEATING OF LARGE ALUMINA PARTS

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The sintering of ceramic material parts by microwave heating at high temperature still remains confined to small parts of the order of a few tens of millimetres. There are, for example, small parts such as dental prostheses in the form of bridges or unitary teeth, or objects of jewellery or small mechanical timepieces. Since we are interested in large parts, problems of temperature control and temperature gradient can occur in the piece during heating and degraded the quality of the piece (cracks, and non-homogeneous microstructures), thus generating variable mechanical properties.

The purpose of this work is to show that it is possible to sinter, by microwave heating, technical ceramic pieces based on alpha-alumina with a large section of 150x150mm^2 and 16 mm thickness, reaching a densification rate greater than 99.5% Dth.

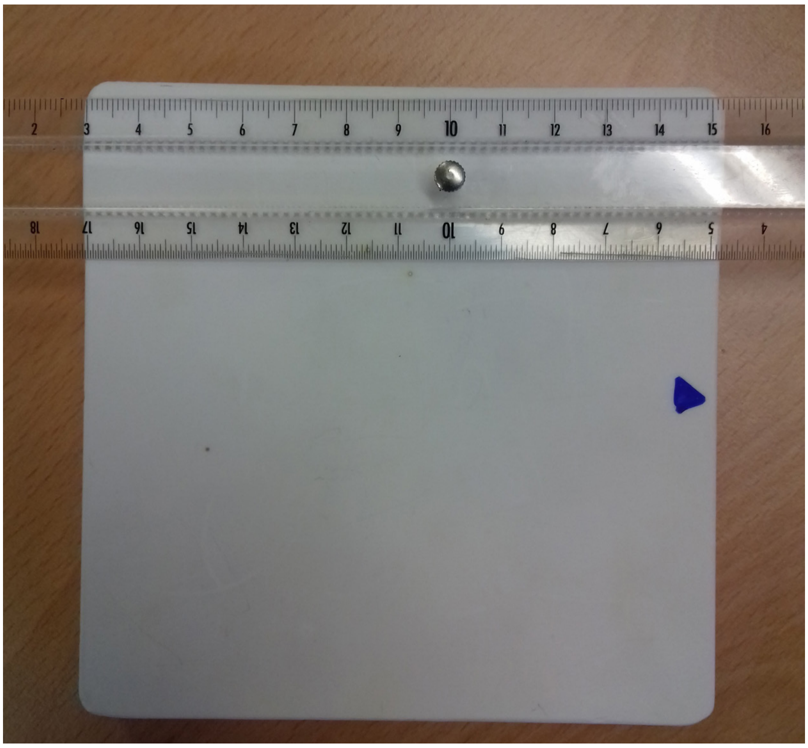
The modelling of the electromagnetic field and the temperature allowed the design of the refractories and susceptors used to confine the temperature and thus to ensure a certain homogeneity of the temperature inside the material. On the other hand, a large experimental study has shown the homogeneity of the pieces obtained.

It is based on the characterizations of:

- the grains size distribution by analysis on images observed by scanning electron microscopy,
- Vickers hardness,
- Toughness by measuring crack length,
- Micro-stress by XRD measurements,

All of these measurements are made both along the thickness and the width of the sintered material.

Keywords: microwave sintering, microstructure, mechanical properties



ABS 42

PHASE-FIELD MODELLING OF NON-ISOTHERMAL GRAIN COALESCENCE IN ADDITIVE MANUFACTURING

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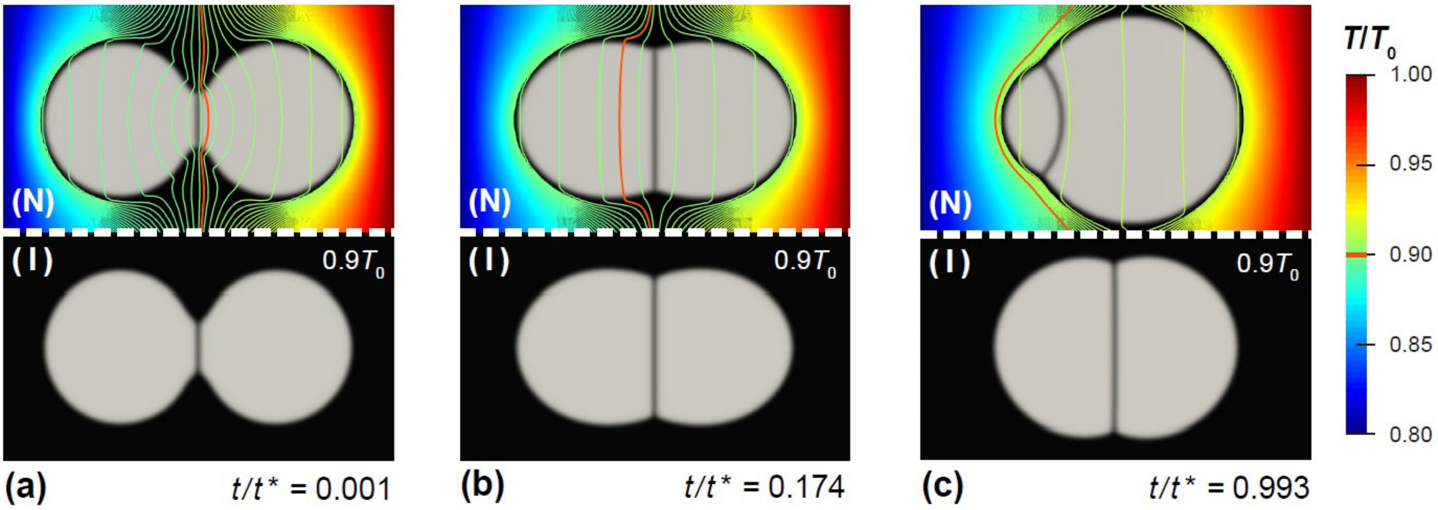
There are increasing interests in the development of new manufacturing techniques for highly efficient and shape-controlled material production, such as the spark plasma sintering, field-assistance sintering and selective laser sintering. These new techniques often possess extraordinary features including local high-energy input, extreme non-equilibrium, fast heating/cooling, high temperature gradient, etc. To improve the understanding of the unconventional grain coalescence process (pore and grain structure evolution) in these new techniques, we developed a non-isothermal phase-field model for the unconventional grain coalescence, as well as its finite-element numerical implementation. The phase-field oder parameters are fully coupled with the temperature field. The parameterization is accomplished by using the experimentally measurable quantities. It is able to capture interesting phenomena which are not accessible to the conventional isothermal model. Thereby challenges such as the temperature-dependent quantities and their interaction with the order parameters, coupling with the thermal process, the difference between the time scale of the thermal process and microstructure evolution will be addressed. The included Figure shows, for instance, how the temperature gradient impacts the sintering of two identical particles, such as breaking of symmetry, in comparision with the isothermal sintering case. Moreover, for the process simulation in additive manufacturing, we will address the numerical challenges on powder bed deposition, power injection and strategies to reduce the computation cost by grain tracking techniques.

Keywords: Phase-field modeling, Sintering, Additive Manufacturing



ABS 950

THE MECHANICAL PROPERTIES AND GAS PERMEABILITY OF SINGLE AND DOUBLE LAYERED PORE STRUCTURE OF LIQUID PHASE SINTERED SiC

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SiC has been most widely used non-oxide ceramics in various industries because of its excellent thermo-mechanical properties such as high strength and hardness, chemical stability under corrosive environment. Due to its excellent chemical and mechanical properties, porous SiC became an attractive material for the vacuum chuck, ceramic membrane, and high temperature dust filter. In this study, various particle sizes of SiC powders were used to fabricate a SiC porous using Al2O3-Y2O3-SiO2 as sintering aid. To obtain uniform pore structure and the distribution of glass phase, Al2O3-Y2O3-SiO2 used for sintering additives were mixed by the ball milling process with Al2O3 balls in ethanol for 24 hours and then dried. SiC powders were mixed with sintering aid powders and PVA solution to fabricate porous SiC green . For the fabrication of double layered porous SiC, filtration layer (less than 30um) was uniaxially pressed at 40 MPa and then support layer was formed on the surface of filtration layer at 30 MPa. For the single layered porous SiC , the green was formed by a uniaxial pressing at 40 MPa. The sintering of SiC porous was proceeded at 1500 celcius degree in argon atmosphere. It was found that SiC porous consisted of YAG phase and residual Al2O3 and Y2O3 phase. With increasing the sintering aid, the flexural strengths of porous SiC were improved from 50 MPa to 68 MPa although apparent porosities were slightly decreased from 45% to 43%. With decreasing the particle size of SiC from 180 um to 15 um, the flexural strength was significantly increased from 15 MPa to 66 MPa, while the porosity of porous SiC was slightly increased from 38 % to 44.8 % and gas permeability gradually increased from 2 to 98 L/min/cm2 at 10 PSI. IT was found that the gas permeability of double layered porous SiC was directly affected by the pore characteristics of porous SiC in the filtration layer. Furthermore, the thickness ratio of filtration layer was found to be significantly influence the gas permeability of double layered porous SiC.

Keywords: SiC, porous, Permeability

ABS 5

MICROSTRUCTURAL STUDY OF SiCF/SiC COMPOSITES DENSIFIED BY CONVENTIONAL AND MICROWAVE ASSISTED CHEMICAL VAPOUR INFILTRATION

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Silicon carbide (SiC) fibre-reinforced SiC matrix composites (SiCf/SiC) have potential for a range of high temperature applications, including hot components in gas turbine engines, fuel cladding and radiation blankets for nuclear fusion reactors. Chemical vapour infiltration (CVI) has been widely used for the densification of SiCf/SiC; the benefits of CVI compared to other approaches including good near-net shape capability and excellent microstructural control. However, the densification of SiC/SiC from conventional CVI (CCVI) is very time-consuming, especially when a large component is required; process times of 1000 hours are not uncommon. This drawback can be eliminated when the infiltration is assisted by microwave heating (MCVI); process times can be reduced to less than 100 hours. In this presentation, the microstructural features of SiCf/SiC produced by CCVI and MCVI will be compared. The phase assemblage and grain growth behaviour of SiC polymorphs in a temperature range of 950-1050oC and a pressure range of 20-70 kPa during CCVI and MCVI were investigated, by a combination of advanced technologies including Raman spectroscopy, X-ray diffraction, electron diffraction and transmission electron microscopy. The influence of a hexagonal BN interface on the SiC fibres on the growth behaviour of SiC grains during CCVI will be reported, together with its impact on the interfacial strength between the fibres and the matrix.

Keywords: SiCf/SiC, Chemical vapour infiltration, Electron microscopy

ABS 4

COMBINED EFFECT OF CONDUCTIVE PHASE AND CURRENT PATTERN ON SPARK PLASMA SINTERING OF Si3N4-BASED CERAMIC COMPOSITE

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The present work investigated the introduced quantity and specific surface area of TiN phase on spark plasma sintering of Si3N4-based ceramic composite. The densification behaviors, alpha-beta phase transformation and microstructure evolution of sintered samples were analyzed and compared between continuous direct current and pulsed direct current SPS processes in relation with the amount and nature of the TiN conductive phase.

By the way of dilatometric measurement and transformed phase calculation, the values of apparent activation energy, which is regarded as an important thermodynamic parameter of sintering, were estimated in both SPS modes. Results indicate that particle size and distribution of the TiN conductive phase have an apparent impact on the sintering behavior and final characteristics of the non-conductive Si3N4 matrix during the current-assisted sintering process.

This systematic study could be meaningful to develop the in-depth understanding of the field-assisted sintering process of Si3N4-based ceramic composites at both the fundamental and the applied levels.

Keywords: Conductive Phase,Current Pattern,Thermodynamic

S03

MODELLING OF CERAMICS

INVITED LECTURES

ABS 804

MECHANICAL MODELLING OF CERAMIC POWDER FORMING AND SINTERING

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An elastic-visco-plastic thermomechanical model for cold forming of ceramic powders and subsequent sintering is introduced and based on micromechanical modelling of the compaction process of granulates.

Micromechanics is shown to yield an upper-bound estimate to the compaction curve of a granular material, which compares well with other models and finite element simulations. The parameters of the thermomechanical model are determined on the basis of available data and dilatometer experiments. Finally, after computer implementation, validation of the model is performed with a specially designed ceramic piece showing zones of different density.

The mechanical model is found to accurately describe forming and sintering of stoneware ceramics and can therefore be used to analyze and optimize industrial processes involving compaction of powders and subsequent firing of the greens.

Keywords: Mechanical Modelling, Sintering, Compaction

ABS 780

ATOMISTIC MODELLING OF GRAIN BOUNDARY SEGREGATION FROM TRANSPARENT POLYCRYSTALLINE ALUMINA TO CALCIUM PHOSPHATE CERAMICS

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Ceramic properties are inherently linked to their chemical composition and microstructure. The use of dopants, which can segregate to both surfaces and grain boundaries during powder synthesis and sintering is a key phenomenon. Using energy minimisation techniques the location, dopant concentration, grain boundary structure and, surface and interfacial energies have been investigated for a number of crystallographic surfaces in YAG [1,2] and alumina for single [3] and copdoped ceramics [4]. These data have then been used in a microstructural model to link these simulations with sintered grain sizes and grain boundary complexions [2-5]. Atomistic modelling of a general grain boundary for Y-La doped alumina has shown very good agreement with high resolution analytical TEM showing a promising future for such simulation approaches [5]. Calculated segregation energy plots and atomistic structure analysis, for the case of trivalent dopants, suggest that there is a critical concentration for achieving the lowest mobility monolayer grain boundary complexion [6]. The bivalent dopant Mg creates ordered arrays of oxygen vacancies at the grain boundary and helps create the space for easier occupation by trivalent dopants in case of codoping. Also twin grain boundaries are more preferable compared to general grain boundaries to obtain monolayer complexions.

More recent molecular dynamics simulation work has focused on bioceramics based on beta tri-calcium phosphate (BTCP) and the first stages of hydroxyl apatite (HA) formation on Ti implants. In the case of BTCP dopants have been seen to influence their dissolution and resorption capacity [7]. Preliminary studies on the validation of the TCP structure and the incorporation of dopants have been made. For the formation of HA on Ti implants several aspects have been investigated – the interaction of simulated body fluid ions [8] and the adsorption of amino acids with a rutile (110) surface [9]. The results show the adsorption of cations onto the negative rutile surface is particularly strong for Ca2+ and weak for Mg2+. For the amino acids the use of metadynamics has led to a clearer picture of the interaction of these Zwitterionic molecules with the rutile surface and possible interference with HAP formation [9].

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Keywords: atomistic simulation,grain boundary segragreation,calcium phosphates

ABS 682

PENETRATION OF CONFINED CERAMICS TARGETS

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We have investigated the penetration response of confined ceramic targets impacted by Tungsten long-rod projectiles in the so-called Lundberg test setup with the ceramic modelled using a mechanism-based constitutive model. The calculations accurately predict the three observed penetration regimes, viz. interface defeat, dwell followed by penetration and penetration with no/short dwell. More importantly, the calculations suggest that these regimes occur in both a ceramic target and a reference target where microcracking of the ceramic is artificially switched off. This is because penetration occurs by a spherical cavity expansion mechanism with the onset of continued penetration set by the attainment of either a critical size of a plastic or damage zone. The dwell time then correlates with the time required to establish this inelastic zone. The main influence of damage is to reduce the pressure required to setup this critical inelastic zone and thereby reduce the interface defeat velocity as well as increase the penetration rate for a given velocity above the interface defeat velocity. We further show that an increase in the downward force due to the backflow of the deforming impactor is not essential for a dwell regime to exist. The mechanism-based ceramic model includes three material length scales and we demonstrate that the penetration size effect reported in experiments is primarily associated the length scale associated with rate dependent lattice plasticity and the critical size of the comminuted zone that is required to trigger granular flow. The material model is also used to probe the dependence of material properties such as strength and toughness on the penetration resistance. Two regimes of penetration, viz. a plasticity-dominated and a microcracking-dominated regime emerge from the calculations. These predictions suggest that increasing the strength rather than toughness of the Corbit-98 Alumina will have a greater beneficial influence on its penetration performance.

Keywords: Dynamic response, Penetration, Ballistic protection

ABS 538

ADVANCED MEASUREMENTS FOR IN-SITU THERMO-MECHANICAL MONITORING OF LARGE SAMPLE UNDER THERMAL GRADIENT (ATHORNA)

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Objective The presented research has been performed in the context of the European project ATHOR (Advanced THermomechanical multiscale mOdelling of Refractory linings) which is primarily dedicated to train 15 Early Stage Researchers in the field refractories for steel applications. This global ATHOR project covers all the main features of thermomechanical behaviours including material characterizations, modelling aspects, and measurements in operating conditions. In order to provide robust quantitative experimental data that can help to validate new modelling approaches, there is a need of improved experimental devices that led us to the development of ATHORNA (Advanced measurements for in-situ THermo-mechanical monitORing of large sample uNder thermal grAdient).

Material & methods ATHORNA aims to develop an instrumented thermal shock bench based on very innovative measurements targeting to in situ monitor the thermomechanical behaviour of a disk shape sample (D about 100 mm) submitted to a thermal gradient. The objective is to suddenly heat (by a CO2 laser) the centre of the front face of the disk of refractory material whose back face is monitored by an infrared camera (tracking of the temperature field) and an optical stereo system constituted of 2 cameras (for accurate tracking of the deformation field). In addition, the occurrence of any cracks (resulting from thermal shock) within the sample is monitored in two ways: on one hand by 6 acoustic emission sensors (distributed peripherally) allowing a spatiotemporal location of the acoustic emission events; and on the other hand by direct measurement of local displacement discontinuities using a suitable refined image correlation technique (2P-DIC).

Results In the multiscale approach mentioned above, a first key point is to optimize the complex microstructure design of a refractory material, in order to achieve exhibits excellent thermomechanical properties (as fracture energy) that would allow to withstand severe thermal shocks. Taking into account those important microstructural aspects, several different materials have been investigated with the ATHORNA device. The obtained of quantitative thermal and strain fields evolutions, as well as of crack initiation and propagation, will be discussed and interpreted in relation with microstructural design.

Conclusions Possibility to compare collected data (temperature and strain fields, location and propagation of cracks) with FEM modelling results under similar conditions, creates opportunity for the ATHORNA device to constitute an essential tool for validation of new modelling approaches. Especially nowadays, these approaches tends to include the non-linear thermomechanical behaviour resulting from complex microstructure of the refractory materials.

Acknowledgements
This research has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement N°764987 and also from Nouvelle Aquitaine Regional Council.

Keywords: Refractory materials, Thermal shock monitoring, Thermomechanical modelling

ABS 387

CRACKING OF CERAMIC ELECTROLYTES DRIVEN BY LITHIUM INSERTION AND SUPPRESSION OF ROUGHENING OF METAL ELECTRODES PLATED BY LITHIUM

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A pre-existing crack in an electrolyte in a battery has lithium inserted into it. If the lithium cannot escape from the crack, pressure will build up and cause the crack to propagate; extension will relax the pressure in the crack, but high pressure will be restored quickly in the longer crack, which will again propagate. This process will continue until the dendrite crack with lithium in it percolates to the storage material in the positive electrode, thereby causing a short circuit. High pressure in the lithium can block the redox reaction that is injecting lithium into the dendrite before crack propagation takes place. The dendrite will then be non-propagating and safe as far as a dendritic short-circuit is concerned.

The roughening of metal electrodes can lead to the formation of dendrites that can cause short circuits. We find that long wavelength perturbations will always increase in roughness. High current densities during battery charging are found to permit growth of the amplitude of small wavelength roughness. The stiffness of the solid electrolyte is found to play a role in limiting the growth of roughness amplitude, but its effect can always be overcome at high current densities and for long wavelength protrusions.

Keywords: ceramic electrolytes, lithium cracking, electrode roughening

ABS 312

EFFECTIVE PROPERTIES OF PARTIALLY SINTERED CERAMICS

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It is well known that the elastic moduli and thermal conductivity of partially sintered ceramics are much below the predictions based on convex pores. It is also widely recognized that the concave pore shape is responsible for these low effective property values. However, the quantitative prediction of the porosity dependence of these properties is still a challenge. In this contribution we first recall that minimum solid area models (minimum contact area models), popularized by Rice and others, are not useful and should be avoided. Then, based on examples obtained for real-world materials, especially alumina and zirconia ceramics, we show that the random microstructure generated by the growth of randomly positioned nuclei, as proposed for elastic properties in the key papers by Roberts and Garboczi, is not always a realistic model for partially sintered ceramics and has to be replaced in many cases by a model based on a maximally random jammed packing of spheres. In the present work the porosity dependence of effective properties has been numerically calculated for these two types of computer-generated concave-pore random microstructures (using the commercial software package GeoDict®, Math2Market, Germany). A comparison of the results shows that the difference is most significant for high porosities, while with decreasing porosity the two data sets approach each other. New ideas for analytical predictions based on the green density of powder compacts are presented as well. Finally, based on a comparison of recent numerical results for random microstructures with overlapping spherical (i.e. convex) pores, concave pores between overlapping spherical grains and microstructures that exhibit transitions from concave to convex pore shape, we show that the Pabst-Gregorová cross-property relation between Young's modulus and thermal conductivity, derived from power-law or exponential relations, provides the best prediction currently available for isotropic porous materials with isometric pores, whether convex or concave or exhibiting transitional shapes between both extremes.

Acknowledgement: Project GA18-17899S, supported by the Czech Science Foundation (GACR).

Keywords: Partial sintering, Elastic properties, Thermal conductivity

ABS 238

THERMAL AND MECHANICAL MODELING OF CERAMIC REFRACTORIES

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In steelmaking industry, refractory ceramics are in contact with molten metal and slag at very high temperature (1550°C) and subjected to intensive thermo-mechanical loads (thermal shock, thermal cycling, ferostatic pressure, mechanisms pressure, slidding) and chemical attacks (corrosion, erosion, gauging, clogging…). These harsh conditions compromise the integrity of the pieces. For safety reasons it is essential to design properly the refractory ceramic pieces and control the pieces behaviour

Finite Element Modelling (FEM) is a powerfull tool to predict the behaviour, improve lifetime and the reliability of the product. But it only makes sence when FEM is properly used with adequate material law to well represent the product in situation of use. Adequate representation of boundary condition is also essential (different step of the process, duration, temperature, contact, interaction, steel throughput….)

In the case of refractory ceramics, which are considered as granular like material, it is necessary to consider the asymmetric behaviour, dependant on the hydrostatic pressure, on time and on the temperature. To evaluate the material, it is primordial to perform dedicated test in different stress states. Those experimental results will be used to identify the parameter of the constitutives equations describing the material law.

The present work will deal with the methodology use to build a material law based on material testing.

Keywords: thermomechanical,modeling,characterization

ABS 172

GROWTH AND PROPERTIES OF CONFINED METAL OXIDES

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The growth of metal oxides with engineered epitaxial strain is now possible. Under these conditions, crystalline thin films that approach the quantum limit have been produced with novel electronic properties. First-principles calculations at the level of density functional theory are useful tools to quantify the way in which the structure of metal oxides changes their electronic properties, including semiconductivity and ferroelectricity. This presentation will discuss several recent collaborative experimental and computational studies of the structure-property relationships of thin metal oxide systems that are strained or otherwise grown through intercalation between confining surfaces. The roles of epitaxial strain, octahedral tilt, and doping on the resulting electronic properties will be discussed.

Keywords: First-principles calculations, Oxides, Interfaces

ABS 53

VIRTUAL PROPERTY COMPUTATION AND DESIGN OF CERAMIC MATERIALS

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The advent of μCT, FIB-SEM and high-powered workstations has made it possible to geometrically model ceramic materials and to compute their properties. This presentation will cover the generation of 3D models based on parameterized statistical models of sintered ceramics. Many metrics can be applied to ensure the validity of the models, i.e. that they agree with reality. Among them are geometric ones like the porosity, pore size distributions and grain size distributions. Other metrics are the permeability, the effective thermal conductivity and effective mechanical properties. For all these, image-based solvers have been integrated into a single software that allow the convenient creation of geometric models as well as convenient prediction of material properties.

With these capabilities, new materials may be developed [1], but one may also use them as alternatives to costly and time-consuming real experiments for the derivation of cross-property relations [2]. Several talks at this event will highlight the latter application of the technology. The capabilities are all available commercially in the GeoDict Software [3].

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Keywords: geometric ceramic models,effective conductivity,effective elasticity

S03

MODELLING OF CERAMICS

ORAL PRESENTATIONS

ABS 834

DISCRETE ELEMENT METHOD (DEM) MODELLING OF WEDGE SPLITTING TEST BY FOCUSING ON THE BRITTLENESS OF QUASI-BRITTLE MATERIALS

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Objective The ATHOR project is an Innovative Training Network (ITN), supported by the European Commission, to build a European multi-engineering research network for Advanced THermomechanical multiscale mOdelling of Refractory linings (www.etn-athor.eu). This study is a part of ATHOR project, which is focusing on the numerical simulation of refractory ceramics by considering their microstructure and its influence on the fracture mechanics. The objective of this study is to develop a numerical tool to simulate the brittleness behaviour for quasi-brittle materials such as refractory ceramics by considering wedge splitting tests. A numerical input parameter is introduced to adjust the fracture energy and brittleness of the material.

Materials & Methods The experimental method that has been used for this study is the Wedge Splitting Test (WST). By investigating the microstructures of the refractories, this test helps to achieve more information about fracture energy and brittleness number. Besides, by combing Digital Image Correlation (DIC), this test can provide the visualization of crack branching.
The chosen numerical method for this study was the Discrete Element Method (DEM). The code that has been used is GranOO which simulates a pseudo-continuum by Cohesive Beam Model (CBM). In fact, the fracture propagation needs a high amount of discontinuities and Finite Element Method (FEM) is not easily capable of managing this kind of microstructure effects. Using DEM to model fracture mechanisms in a continuum media, especially in the ceramics field, is a new approach and it is still under intense development.

Results The introduced parameter is based on the local fracture criteria of the discrete element beams. For driving the brittleness of the material, this fracture criteria inside the sample followed a uniform random distribution. Subsequently, the impact of randomization of local fracture criterion of the discrete element beams on the brittleness of the material is studied. Interestingly, the range of randomization plays a vital role in adjusting the overall fracture energy and the brittleness number of the material. Indeed, this numerical process could represent the effect of pre-existing cracks within the microstructures.

Conclusions Increasing the randomization range from the mean fracture criteria, in the sample's discrete element beams, results in higher overall fracture energy in the sample. Hence, by using the introduced approach, it is possible to adjust and calibrate the fracture energy and the brittleness of the materials in numerical models.

Acknowledgements: This work was supported by the funding scheme of the European Commission, Grant Number: 764987.

Keywords: Discrete Element Method, Fracture Mechanics, Brittleness of Materials

ABS 827

ACOUSTIC METHOD FOR EVALUATING THE PERMEABILITY OF BONE-LIKE BIOACTIVE GLASS-CERAMIC SCAFFOLDS

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Objectives In tissue engineering (TE), structural parameters can strongly affect the performance of porous scaffolds used as templates for supporting tissue ingrowth and regeneration. The aim of this study is to evaluate the effect of thermal treatment (sintering) on inter-pore interconnectivity and intrinsic permeability of glass-ceramic scaffolds for bone TE by making use of a simple and highly-reliable acoustic method.

Materials and methods Cylindrical silicate glass-ceramic scaffolds with porosity above 64 vol.% were produced by foam replica method [1]. The green bodies were sintered at Ts = 600, 650 and 700 °C for 3 h in an electrically-heated furnace. The intrinsic permeability k (m2) was determined in the linear Darcy's region by using an acoustic system based on a single-pressure transducer [2]. A slow alternating air flow was generated within a close volume by a piston moved by a stepper motor. The sinusoidal pressure component was measured and the output data were processed through a spectrum analyzer. Statistical analysis was performed to determine the expanded uncertainty related to geometrical factors. Morphological analyses were performed by scanning electron microscopy and micro-computed tomography to evaluate the pore-strut architecture of the scaffolds.

Results The porosity of the scaffolds decreased from 75.7 to 64.5 vol.% as the sintering temperature increases from 600 to 700 °C due to the higher densification of the structure. The permeability values k varied from 5.23×10-12 to 1.3×10-10 m2 for Ts = 600 and 700 °C, respectively. These values are comparable to the typical ones of human cancellous bone [3]. Interestingly, it was found that k-values decreased as Ts increased following a linear trend (R2 = 0.9998).

Conclusions The determination of the intrinsic permeability of sponge-replicated scaffolds was successfully carried out. This study proved the high reliability of the method in terms of experimental repeatability and accuracy, thus making it very suitable for the structural characterization of TE scaffolds.

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Keywords: Bioceramics, Scaffold, Porosity

ABS 817

PHASE FIELD MODELLING OF GRAIN GROWTH UNDER ELECTRIC FIELDS: APPLICATION TO THE SPARK PLASMA SINTERING

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This presentation reports the phase field modelling of a 3D microstructure of ceramic grains subjected to DC and AC electric fields. The time microstructural evolution will be described as function of the electric field intensity and frequency.

The role of the grain boundary electrodynamics on the grain size distribution and the textures will be carefully addressed.

Keywords: Grain growth, spark plasma sintering, Phase field

ABS 773

MODELING OF ELASTIC MODULUS EVOLUTION IN POROUS CERAMICS DUE TO THERMALLY INDUCED CRACKING

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Within polycrystalline porous ceramics used in automotive applications as diesel particulate filters, it is evidenced that during cooling from firing temperature micro cracks are gradually formed. The cracks are formed as a consequence of strong thermal anisotropy of grains. Typically these micro cracks are granting better thermal shock resistance, with respect to dense materials, but reduce stiffness. The reduction can be quantified by measuring the drop in elastic properties of bulk material which, depending on the level of porosity, can decrease even by 50% with respect to its value at high temperature. It is further observed that upon subsequent heating these cracks are closing and partially or totally healing at very high temperatures. Such peculiar behavior results in partial or complete recovery of the elastic properties of bulk material upon completing one thermal cycle. Despite its evident practical application, still there is no constitutive description of this phenomenon, capable of predicting the evolution of Young's modulus as a function of temperature history. For reliable numerical simulation of this phenomenon, it is required to model fracture. To model inter-crystalline fracture, an effective strategy is to use cohesive elements, since crack patterns are a priori known. Major limitation of this approach is that the cohesive elements already implemented within commercial codes cannot take into account crack healing upon subsequent heating. In this study new cohesive element is developed and numerically implemented within ABAQUS commercial finite element code, capable of modeling both crack opening, closing and healing. Further on, a computer code is generated to build numerical model of porous ceramic specimens that takes into account experimentally measured crystallographic orientation and porosity, and models the microstructure by using Voronoi polygons. The developed numerical tools serve as a framework for more realistic simulations, required to study the hysteresis in elastic properties within porous ceramics provoked by thermal cyclic. In a subsequent phase, an inverse analysis procedure is developed, in which macroscopic properties are used to calibrate parameters entering into micro crack model. The approach is centered on a minimization of a discrepancy function designed to quantify the difference between experimentally measured quantities and their computed counterpart. The model is calibrated on the basis of experimental data regarding the drop of bulk Young's modulus with decrease of temperature. Developed procedure is tested with porous cordierite sample, and obtained results are quit promising despite the current limitation of using only two-dimensional model.

Keywords: Thermal cyclic hysteresis, Cohesive cracks, Inverse analysis

ABS 752

RECONSTRUCTION AND VALIDATION OF THE MICROSTRUCTURE OF THE REAL ZIRCONIA TOUGHENED ALUMINA CERAMIC COMPOSITE

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The capability of accurately predict the properties of composites through the use of predictive methods could drastically increase the efficiency in the development of novel ceramics with innovative and improved applications. The literature is consensual relatively to the adequacy of the application of Voronoi tessellations to reproduce the materials microstructure due to the combination of the simplicity of formulation and the high representativeness of the results.

In this work, a reconstruction of 3D microstructure of a real zirconia toughened alumina (ZTA) ceramic composite are generated through the use of open source Neper. In order to validate the 3D theoretical microstructure the elastic modulus was determined and an innovative approach was carried out in order to understand the effect in the numerical simulations of the size of representative volume cell, sphericity and distribution of the grains and its spatial arrangement.

Constituent phase properties such as the volume fraction, grain size distribution and shape were used as input in order to generate full dense microstructure of a ZTA in different volume fractions (5%, 15%, 22% and 40% of zirconia). Scanning Electron micrographs were analyzed using ImageJ software and at least seventy representative grains was measured of each phase. Scheil-Schwartz-Saltykov method was applied to obtain information concerning to the distribution diameters of 3D grains. After that, the finite element method commercial software Ansys was used to perform the required analysis and implement some post-processing scripts using Ansys Parametric Design Language to obtain the value of the elastic modulus.

Numerical results for ZTA emphasize some relevant conclusions namely, from the 3 representative cells used (edge length of 2, 5 and 8 μm) the first one reveals unappropriated once results present significant variations and far from experimental ones. The other two sizes larger show a sufficient representation of the real microstructure since the greatest difference observed between the numerical and experimental results was 5%. Besides the visual aspects of the cell without sharp edges and the improve mesh quality, the influence of the sphericity in elastic modulus is not significative. The same effect is also visible in size distribution of the grains, where the variation of the standard deviation keeping the average value show negligible changes. From the spatial arrangement of grains, keeping the same size distribution, it was concluded that its influence is not significant once variation in elastic modulus is smaller than 0.4%.

Keywords: Microstructure Reconstruction, Numerical Modelling, Elastic Modulus

ABS 747

DETERMINATION OF THE SHEAR VISCOSITY IN MESOSCOPIC SIMULATIONS OF CERAMIC COLLOIDAL SUSPENSIONS

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In the field of ceramic processing, there has been recently a growing interest in developing colloidal processes for example based on additive manufacturing. In such processes, it is crucial to understand and control the rheological properties of dilute suspensions not only to assure a good flow but also to obtain specific physical properties related to the colloidal arrangement. Given the large number of parameters playing on the colloidal behavior, numerical suspensions performed at a mesoscopic level (particle scale) appear as an interesting tool to discriminate the role of each parameter. However, to describe correctly the rheological behavior of suspensions in simulations, it is important to take into account the hydrodynamic interactions and to have a good description of the particle sizes.

To show this, we will use a reverse non-equilibrium molecular dynamics method (RNEMD) of Müller-Plathe [Phys. Rev. E, 1999, 59, 4894] to determine the shear viscosity of hard sphere suspensions in SRD-MD (« stochastic rotation dynamics-molecular dynamics ») simulations, which allow to describe hydrodynamic interactions in colloidal suspensions. We will particularly focus on the differences obtained with different coupling schemes that can be used in SRD-MD and which do not describe the hydrodynamic interactions and the particle size with the same accuracy.

Keywords: SRD-MD simulations, shear viscosity, colloidal suspensions

ABS 734

FIRST-PRINCIPLES CALCULATION OF CRYSTALLINE PRECIPITATE PHASES M23C6 (M = CR, W, MO, FE) IN NI-BASED SUPPER-ALLOYS

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The presence of precipitate phases M23C6 (M = Cr, Fe, Mo and W) plays significant role in the strength and creep resistance of Ni-based superalloys. These complex crystalline carbides have 116 atoms in the cubic fcc lattice. We report the investigation of the electronic structure, interatomic bonding and mechanical properties for eight binary phases of M23C6, and M23N6 and six ternary phases of (M1, M2)23C6. Based on the results obtained, we conclude that Fe makes the crystal less stable and lowers its cohesion whereas W makes the material more compressible. Apparently, the root of these observation is related to the size of the metal ion and the complex interatomic bonding of C atom with 3d electrons in the metals. Moreover, Cr23C6 is confirmed to be the most prominent precipitate phase with superior overall physical properties. Such information shed much light on carbides stabilization in Ni-based superalloys.

Keywords: Cr23C6 precipitate [hases, DFT calculations, Ni-superalloys

ABS 681

LINK BETWEEN MICROSTRUCTURE AND COMPRESSIVE STRENGTH OF LIGHTWEIGHT GYPSUM

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To reduce energy cost of manufacturing and transport, weight reduction of construction materials is a solution. In our case, a compromise between density and mechanical properties of lightweight plasterboards has to be found, particularly for its core material: lightweight gypsum. Mechanical requirement in terms of local resistance are indeed crucial in this case. Understanding of the relation between structure and mechanical properties is hence essential.

Lightweight gypsum contains three levels of porosity: macropores (around 500 µm) obtained by foam introduction, mesopores (around 50 µm) due to hemihydrate particles dissolution and micropores (around 1 µm) created during gypsum crystallization. This microstructure is observed by X-ray tomography where only macro-porosity and mesoporosity are visible with a voxel size of 2 µm.

A method of image analysis has been developed to inspect foamed gypsum microstructure. After segmentation, coalesced pores are separated and their equivalent diameters are measured with 3D watershed technique. Homogeneity of the porous phase is also characterized using the minimum path algorithm. It involves the calculation of the most energy saving path (or minimum path) for a fracture coming from one side of a 2D image to its opposite side. This algorithm is applied repeatedly on several slices of the volumes scanned with a 15 µm voxels resolution. The mean value of minimum path cost gives an indication on the homogeneity of the macroporosity.

Tomography also allows conducting in situ tests of spherical indentation (see Figure). Displacement fields are measured by digital volume correlation in order to study and identify the material mechanical behavior [1]. Residuals fields are also helpful to study the damaged zone under the indent (shape, volume and densification). From this in situ indentation tests, displacement fields and gypsum microstructure are used as input data in this finite element modelling. The actual microstructure is meshed and the two visible level of porosity are taken into account into the finite element model. The aim is to understand the behavior of the transition zone between the damaged and the undamaged material.

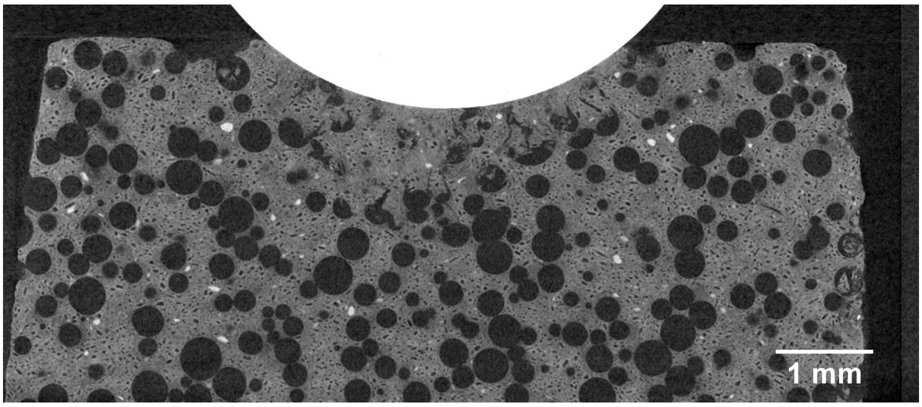

Figure: In situ indentation test of foamed gypsum with a 6 mm diameter hard ball

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Keywords: Gypsum, X-Ray tomography, In situ spherical indentation

ABS 640

DIGITAL TRANSFORMATION IN THE CERAMICS INDUSTRY - A VIRTUAL VIEW INTO YOUR SINTERING PROCESS BY THERMOKINETIC SIMULATION

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Introduction The most time-consuming step in ceramic manufacturing – in which the green becomes a dense ceramic at high temperatures – is sintering.

The **objective** in this step is to obtain the highest quality with minimal energy consumption in a short time.
During a process, different procedures occur simultaneously:
Grain size diffusion
Surface diffusion
Lattice diffusion
Phase transitions
Depending on the local temperature, particle size and atmosphere, the process with the highest rate dominates. The temperature program for a process is difficult to predict. What occurs at which point in time and at which temperature, can be understood by means of thermal analysis methods.

Thermokinetic Simulation - a look into the kiln through a 'virtual door":

Based on measurements, carried out with different heating rates, KINETICS NEO by NETZSCH is able to calculate a digital reaction model of debinding and sintering processes. If the model fits the real measurements, process engineers can apply any kind of virtual firing programs to the software and simulate the conversion steps for every reaction step.
Areas in the firing program, where no conversion takes place can be speeded-up. Areas with too high conversion rates can be changed to lower conversion to avoid damage.

Conclusion Examples from the industry show, that simulation can speed-up a firing process up to 60%. That means
- Lower energy consumption
- Faster processes
- Less test-fires
- Less scrap
- Faster time to market

KINETICS NEO brings the scientific approach of thermokinetic simulation on a usability level for the daily use in the industrial environment. It provides a virtual view of the sintering process.

Keywords: Sintering, Simulation, Digital Transformation

ABS 629

EFFECT OF CREEP ON REFRACTORY MASONRY WALL SUBJECTED TO HIGH TEMPERATURE

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Refractory masonry in its application is usually exposed to chemical, thermal and mechanical loads in service. Mechanical loads develop from the thermal expansion of the refractories which is confined either by the regions of different temperature within the structure or by the boundary conditions. The aim of this work is to investigate, using numerical simulation, the influence of creep on the thermomechanical behaviour of the refractory masonry and the identification of failure mechanisms arising from the high temperature loadings. Different modelling approaches are used and coupled with the most advanced constitutive models available in commercial software in order to produce thorough parametric and sensitivity studies. Investigation is specially focused on the adverse effect of creep on stability of the masonry wall. The comparison is carried by taking consideration of creep effect and without creep effect.

Keywords: Numerical modelling, Thermomechanical behavior, Parametric analysis

ABS 618

NUMERICAL AND EXPERIMENTAL THERMAL ANALYSIS FOR DIRECT AND HYBRID MICROWAVE HEATING

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Sintering process is a step of powder metallurgy consisting in the densification of pulverulent materials. This densification is achieved by thermo-activating diffusion mechanisms, while remaining below the melting point. Usually, sintering of ceramics is carried out using conventional heating. However new heating techniques have been developed in recent decades. Among these techniques, microwave heating is known [1,2] to be volumetric, to reduce energy consumption and processing times. Another interesting feature of microwave heating is that it is selective. In this context, the objective of this work is to compare numerical simulations of alumina (Al_2O_3) heating with experimental data in two configurations: direct and hybrid (indirect) heating. Indeed, the temperature field in the bulk materials is a key parameter controlling subsequent densification.

Using an experimental set-up composed of a 2.45 GHz monomode cavity, measurements of temperature response are performed for different applied powers and configurations – silicon carbide (SiC) only - Al_2O_3 only - SiC and Al_2O_3. This last case corresponds to a hybrid heating, where SiC acts as a susceptor due to its higher permittivity values. In all cases, numerical simulations are required to determine the distribution of the temperature in bulk. These computations are carried out using the finite element solver COMSOL MultiphysicsTM software. In addition, such simulations are a way to test the reliability of known values of material permittivity, a quantity difficult to obtain.

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Keywords: microwave heating, finite element method, sintering

ABS 541

A MESOSCALE MODEL OF FACETED TITANIA FILM GROWTH

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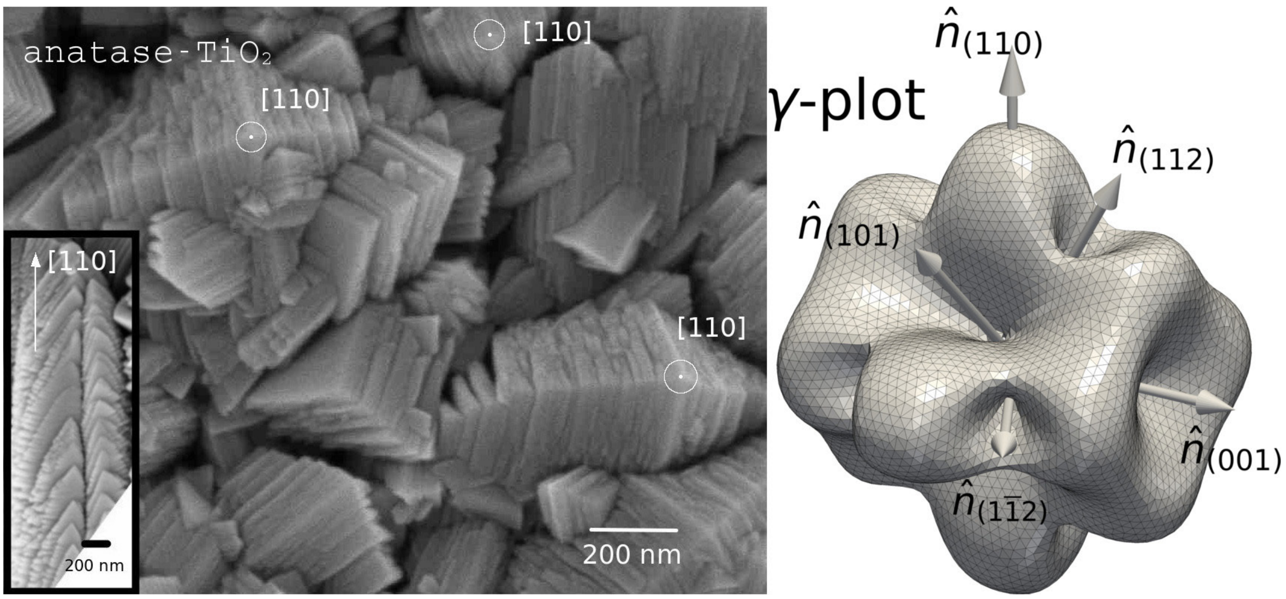
Controlling the interfaces, including the free surfaces, of thin films is of crucial importance for applications such as photocatalysis, energy materials and environmental barrier coatings. A novel, polycrystalline, titania film grown by chemical vapour deposition possesses unusual anatase dendrites with plate-like secondary features, see Figure left, and has demonstrated excellent photocatalytic and antimicrobial activity. The striking morphology corresponds to a [110] growth direction, and the activity is thought to be related to the crystallography of the exposed surfaces and nanostructure. The unusual microstructure is hypothesised to result from the interplay between shadowing due to ballistic deposition at low pressures and anisotropic surface diffusion driven by surface energy during deposition. There is no existing modelling framework to explore these detailed questions.

In this work, we focus on the formation of the kinetically frozen facets and employ a phase-field model to incorporate both process-specific and materials-specific effects. The non-local deposition process is realized by coupling the ballistic flux to the surface with the energy minimising formulation of surface diffusion. Anisotropic interfacial energies for anatase, see γ-plot in Figure right, employ ab initio-derived energies in the Siem-Carter construction. The surface morphology and crystallography at various stages of film growth and analysis of surface roughening exponents can be obtained naturally, and will be compared to experimental results.

The strongly anisotropic surface energy in the phase-field formulation results in a 6th-order non-linear PDE, which is known to be challenging to approximate numerically. To this end, we employ an efficient stabilized time integration scheme in combination with a pseudo-spectral method. A fast direct solver based on a matrix diagonalization method for the spectral discretization is implemented. The solver is readily parallelized and can be applied to the large-scale simulation of our complex 3-D microstructures.

The modelling and analysis here will enable engineering of film growth conditions to obtain optimal performance of these titania films. It will provide insight into the controlling processes that result in active surfaces. This novel modelling approach can be extended to other thin film vapour growth processes such as sputtering, plasma deposition and diffusion limited aggregation.

Keywords: chemical vapour deposition, phase field model, thin film



ABS 526

WETTABILITY IN THE ELECTRODE OF LITHIUM-ION BATTERIES

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Wettability by the electrolyte is claimed to be one of the challenges for the development of high performance lithium-ion batteries (LIBs). Non-uniform wetting leads to irregular reaction and unstable formation of solid electrolyte interface film. Incomplete wetting influences on the cell performance and formation of lithium plating in the anode that causes safety issue. It has been pointed out in the literature that the insufficient wetting can be found in the electrode and the electrolyte transport phenomena are different in the cathode and anode. In this study, we use lattice Boltzmann (LB) simulation to show the electrolyte distribution and electrolyte saturation to understand the wetting characteristics in the cathode and anode. We develop the multiphase LB model by reconstructing the electrodes with stochastic generation method. Our result should lead to more reliable LIB design, and provide a framework to inspect the wettabilities inside the electrodes.

Keywords: Wettability, lithium ion batteries, lattice Boltzmann method

ABS 450

A STUDY OF SANDBLASTING PROCESS BY NUMERICAL MODELING AND EXPERIMENTAL APPROACHES

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Substrates surface rugosity is a primordial parameter of thermal spray coatings formation and its adhesion. Its effect is linked to the contact surface that the molten particle establishes during its flattering on the substrate [1]. Mellali et al [2] have shown that anchoring is mainly mechanical. This phenomenon goes through the splats contraction during their cooling around rugosity pics. Such mechanism requires the existence on the substrate surface of anchorage spots, which are created by sandblasting. The treatment's resulting rugosity must be controlled and adapted to the sprayed particles sizes.
Previous studies have shown that most surfaces preparations modeling referred to stresses induced by shot peening: impacts of spherical, metallic and fixed radius elements were then considered. Nevertheless, sandblasting relied on impacts of angular ceramics particles of variable sizes. To our knowledge, studies that covered both experimental field and simulation are quite rare. Therefore, this work will highlight and introduce a realistic finite element model that describes the mechanical effect of soft sandblasting process. The major work behind this research was to emphasize on the resulting surface morphology and the residual stresses in the material depth. Finally, a comparison between the numerical work and the experimental data will be discussed as well as the major parameters influencing the deposit characteristics.

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Keywords: sandblasting, finite element analysis, residual stress

ABS 330

BaTiO3-CERAMICS AND GRAIN GROWTH ENGINEERING USING FRACTAL NATURE APPROACH

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Grain size and morphology of BaTiO3-ceramics are very important characteristics in developing new dielectric devices. Samples with different additives were sintered at different temperatures and times. The microstructure of the samples was observed using scanning electron microscope (SEM). Experimental results indicated well-developed morphology of BaTiO3-ceramics from nano- to micro- scales, with the standard ceramics consolidation procedure. It is observed that the morphology of grains is the function of additives, sintering temperature and sintering time. However, image analysis of grain growth indicated that sintering temperature has a strong impact on the morphology and grain size of the samples in the temperature range 1240 °C to 1380 °C. Kinetic exponents and grain growth fractal dimensions were obtained with the collecting the parameters of same grain exposed to five magnifications by SEM imaging and using appropriate processing software for grain-shape fractal reconstruction. The main results in this paper established the relation between sintering consolidation process and fractal nature influence, as well as complex fractal correction on sintering temperature.

Keywords: BaTiO3-Ceramics,Grain Growth, Fractal Nature

ABS 357

RHEOLOGICAL STUDIES ON CERAMIC PASTES FOR NUCLEAR FUELS EXTRUSION SHAPING

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To this day, nuclear MOx -(U,Pu)O2- fuels, have been shaped into pellets by dry-pressing a mix of UO2/PuO2 . This process relies on several steps, among which the materials are powdered (crushing, mixing, sieving, pressing). It presents proven benefits, such as ease of implementation and high production rates. However, shaping processes based on materials in a wet or liquid state, are interesting alternatives for the mixing steps and tackle some of their drawbacks. Indeed, they reduce the dust accumulation due to dry-powder handling. Moreover, such processes should improve sintered fuel microstructures, through a more homogeneous mixing in the first steps. Extrusion processes could prove useful to engineered fuel rods. This work is focused on understanding the rheology of ceramic pastes, to be able to control its extrusion.

To ease initial works, yttrium oxide and titanium dioxide powders, acting as equivalents of plutonium dioxide and uranium dioxide, were selected for their respective similarity regarding morphology, granulometry and electric neutral point in suspension. These criteria being the main parameters physically dictating the agglomeration and flow of the ceramic pastes. The pastes were obtained with a 30cm3 roller blade mixer (Brabender). Organic additives were added to enable the extrusion of non-model, highly charged systems. A capillary rheometer (RH2000, Malvern Panalytical) and less-conventional squeeze test flows were used to study the rheology of such pastes. A ram-extruder was built and mounted on an electromechanical testing machine (Instron).

Ceramic pastes, shaped into 20cm rods, without surface defect and withstanding the specifications for nuclear fuels were further characterized. The extrusion pressure is shown to be well predicted by Benbow-Bridgwater's equation when changing geometry and speed. Constitutive modelling has been carried out on the forces obtained from squeezing test set-ups. The compressive forces were found to be dependent on sample deformation, compressive speed and volume fraction of ceramics. Bulk and wall friction seems to play an important role in flows of the system studied. Traditional capillary experiments have also been found to be poorly reliable to successfully characterize the rheological behavior of these complex systems.

Extruding highly charged ceramics rods, under nuclear specifications, is challenging. Modelling such flows requires reliable rheological flow-configurations. Squeezing tests and modified models successfully predict these pastes behavior under controlled flow conditions. Further work will focus on applying these revisited models on extrusion flows. The final goal will be to transpose the study on ceramic pastes with nuclear oxides.

Keywords: Rheology, Squeeze-test, Extrusion

ABS 320

THERMOMECHANICAL CHARACTERIZATION OF ALUMINA SPINEL BRICKS

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The modelling, design and optimization of refractory masonry structures requires the fully understanding of its thermomechanical properties. The state of the art regarding the thermomechanical characterization of refractory ceramics are presented, as well the most used techniques for the determination of their thermal and mechanical properties.

The mechanical properties of alumina spinel bricks are been investigated by compressive tests, performed at cylindrical samples extracted from the bricks to generate its compressive strain-stress curves at room temperature, 600ºC, 800ºC and 1.000ºC. The tests will be done under displacement the control 0,01 mm/s. The samples have 51 mm in diameter and 130 mm in height. An electric split furnace will be used to heat the samples at the constant rate of 5ºC/min. The strains will be measured using a strain gage at the opening of the furnace and the displacement given by the press will monitored. A 200 kN press with an electromechanical jack will be used to apply the compressive load.

The test results are the compressive strain-stress curves of the material. It will be possible to identify the compressive strength of the material at room temperature and the compressive strength at a given temperature. The strain corresponding to fc and the rupture strain may also be determined for each temperature.

The compressive strain-stress may be used for modelling, once they represent the damage plasticity of the material This research will generate experimental results that will be used for calibration and validation of numerical models. Once the models are validated, they will be used to optimize the design of refractory masonry used at steel ladles.

Keywords: Refractory Materials, Thermomechanical, Characterization

ABS 284

EXPERIMENT AND SIMULATION OF THE FORMATION OF GREEN BODIES FROM ALUMINA POWDER

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Creating nearlyconstant density and residualstress fields throughout the entire green is necessary for producing highquality, highperformance ceramics consistently. The use of computational tools for virtual prototyping of molds and processes help to accelerate development and decrease costs. The possible benefits are particularly advantageous for the production of large green bodies with complex geometries. The present research introduces a novel constitutive model for ceramic powder compaction and includes: a new formulation for elastic behavior of the powder phase, a reformulation of the compaction law, and an elastic stiffening. This new computational model is calibrated on uniaxial compaction (disk forming) and triaxial compression experimental data for Martoxid KMS 96 alumina powder. Once the model has been calibrated, the parameterization is used to predict the compaction behavior of the alumina powder in the formation of green bodies.

Keywords: Powder compaction, Modelling, Virtual prototyping

ABS 278

UNDERSTANDING THE ELASTIC AND THERMAL RESPONSE IN PRINCIPLES AND MECHANICAL STUDIES

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The interest and development of two-phase ceramic-metal composites (cermets) with potential biomedical, aerospace and automotive applications has been an active field of research in the last few decades [1,2]. Carbide-based ceramics, such as titanium carbide (TiC), are common components in many hard, wear resistant cermets. These materials have excellent properties such as high hardness, chemical inertness, high thermal conductivity, and a high melting temperature. The desired properties of the cermets are also controlled through the addition of ductile metallic binders, such as elemental or alloyed Ni, Fe, or Co, and more recently nickel aluminide intermetallics (Ni3Al). However, for a number of reasons, many studies have an incomplete understanding of the influence of the atomic structure of these composites in relation to the roles of the constituents, the optimal ceramic-binder ratios, and their ultimate mechanical and thermal characteristics. In these terms the investigation on the exact mechanism responsible for the cermet's mechanical behaviour at ambient and elevated temperatures is important. Using first-principles calculations and experimental studies, the present work benchmarks the results obtained for TiC-Ni3Al cermets to the individual TiC and Ni3Al components (as well as their elemental constituents), in an effort to predict selected fundamental mechanical and thermal properties of these composites, as originated in atomic composition and structure. The first-principles calculations were conducted in terms of Density Functional Theory as implemented in VASP software package (URL http: //www.vasp.at), while experimentally obtained plastic, elastic and thermal responses were accessed through the use of hardness-indentation test, ultrasonic pulse-echo method, and dilatometry studies, respectively. Our results show that the theoretical calculations are in good agreement with the measured experimental data for the many different parameters examined and calculated, notably elastic properties, thermal expansion coefficients, and selected structural properties.

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Keywords: Cermets, Ab-initio, Titanium carbide

ABS 254

IONIC CONDUCTIVITY OF DOPED-HfO2: 1 CORRELATION BETWEEN EXPERIMENTAL AND DENSITY FUNCTIONAL THEORY CALCULATIONS

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According to European regulations, new « green monopropellant » must be developed to replace the toxic hydrazine-based fuels for satellite propulsion. The research concerns a monopropellant formulation offering optimized physical-chemical properties and unparalleled propulsive performance. This gain in performance results in a significant increase in the temperature of gases (3000 K) in the combustion chamber, which in turn must be protected. Thus, our aim is to develop a new ultra-high-temperature material able to sustain the high temperature and oxidizing environment.

Functionally graded materials are good candidates for this application. They can be built of a metallic part associated with a thermal/environmental barrier. Hafnia (HfO2) has been chosen for the barrier component. However, it has to be stabilized in its cubic high temperature structure to avoid destructive phase transition during temperature cycling in service. The stabilization is obtained by doping with rare earth oxide (RE2O3) in the right proportion. However, the presence of rare earth induces oxygen vacancies, which play a crucial role in increasing the ionic conductivity, a behavior which must be characterized, understood and finally controlled.

Previously, the effect of the amount of yttria (Y2O3) as dopant on the ionic conductivity was investigated. Considering only the cubic phase, ionic conductivity decreases with the increase of the doping rate. Several parameters influence the ionic conductivity (oxygen vacancies, mobility) such as the ionic radius (RE3+) and, the volume fraction, the molecular weight and the enthalpy of formation of the dopant (RE2O3). This study is focused on the influence of various dopants (Gd2O3, Lu2O3) on the ionic conductivity at high temperature in air and water vapor.

In parallel, Density Functional Theory (DFT) is used to study the relative stability of the allotropic phases of perfect structures of pure HfO2 and doped HfO2. Then, vacancies and dopant are added to the model to study the oxygen mobility and so the ionic conductivity of the material.

Finally, correlation between DFT calculations and experimental data permits to determine a promising composition of the thermal barrier.

Keywords: DFT, Hafnia, ionic conductivity

ABS 235

STRONG METAL-SUPPORT INTERACTIONS BETWEEN METAL AND OXIDE NANOWIRE THIN FILMS

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From painting, biocompatible coatings, solar cells, memristors to environmental purification, titanium dioxide (TiO2) has a plethora of applications and is one of the most studied oxide material in the last decades (1, 2, 3). In most of these applications, titanium dioxide is used in the form of nanoparticles. The coarsening behaviour of nano TiO2, mainly because of recent studies almost exclusively addressed to the coarsening of these, nearly spherical, isotropic nanoparticles is well understood. Indeed, the degree of the particle anisotropy might induce a strong shape-dependent variation in properties of matter, which raises the question how the coarsening of anisotropic particles proceeds at various interfaces.

In this study coarsening behavior of 2D thin films and individual titanate nanowires coated with few nanometer thick Au thin film were studied by using various electron microscopy and surface probe techniques. We followed in situ and ex-situ in transmission electron microscopy the temperature dependent structural and geometrical evolution of ceramic/noble metal interfaces down to the single particle level (4, 5).

We have observed a remarkable stabilization of the smallest noble metal nanoparticles on the edges of titania nanowires which may be the consequence of combination of a strong metal support interaction effect (SMSI), formation of Ti3+ defects or geometrical constrains.

Understanding the sintering behavior of 1D oxide nanowires and metal nanoparticles will open up new routes to design efficient heterogeneous catalyst and photocatalyst systems.

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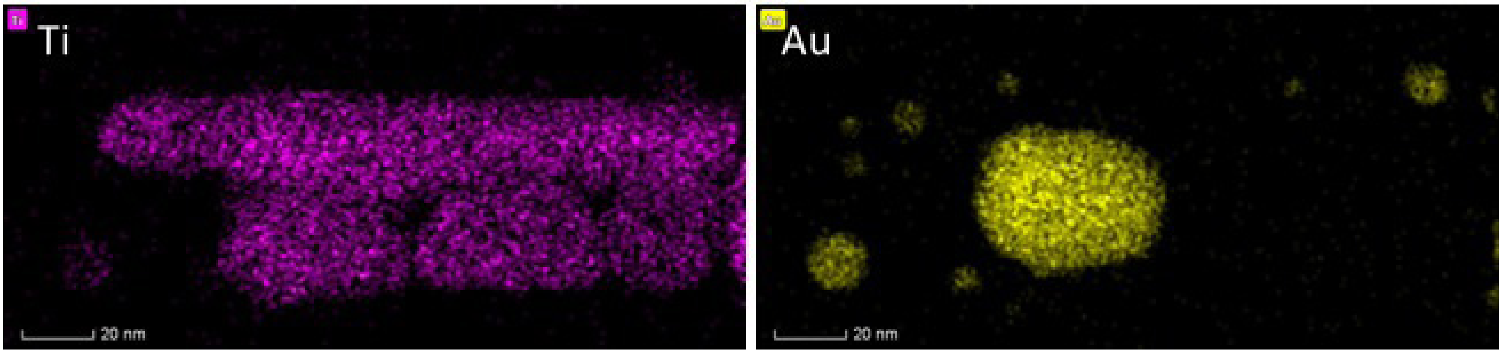
Keywords: Titanate nanowires, Sintering, Surface area



ABS 944

TOWARDS UNDERSTANDING THE SURFACE MECHANISM OF THE COLD SINTERING PROCESS: A COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY

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The Cold Sintering Process (CSP) is a unique protocol developed to obtain high-density ceramics at low temperatures (<300 C). This protocol has been applied to densify a wide variety of materials successfully. The CSP benefits aqueous solutions to assist the densification of material through dissolution and precipitation/recrystallization processes. Differently from other sintering techniques, in CSP, the free energy is lowered at the interfaces through hydrothermal reactions. This study combined computational and experimental work to study the interfacial reaction kinetics during the precipitation/recrystallization in CSP. The computational studies were performed using molecular dynamics simulations with ReaxFF, a reactive force field which is capable of modeling large atomistic systems with reactive events for long simulation times. The acetic acid/water/zinc oxide interfaces were investigated for a variety of pH values (i.e., acetic acid concentrations). The simulation results show that the pH of the solution used during the dissolution in CSP affects the crystallization. Furthermore, depending on its concentration, the presence of an excess amount of acid prevents the diffusion of dissolved material into pores which is validated by experiments. The presence of water is not only facilitating atomic diffusion after dissolution but also creating a vacancy-like structure on the surface through hydroxylation which enhances the surface diffusion at low temperature. This mechanism explains the extraordinary grain growth after the evaporation of excess water in the system.

Keywords: Cold Sintering Process, ReaxFF, Zinc oxide

ABS 154

COMPARISON OF MOLECULAR DYNAMIC SIMULATIONS OF SHOCK RESPONSE AND AMORPHIZATION OF BORON CARBIDE WITH EXPERIMENTAL DATA

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Boron Carbide is an advanced structural ceramic with high hardness (~30 GPa), high compressive strength (5 uGPa) and low density (2.52 g/cm^3). Although boron carbide exists in rhombohedral crystal structure, it also exhibits polymorphism where the atomic arrangement of boron and carbon atoms can vary in each unit cell, and stoichiometric variation of carbon to boron ratio can vary from 13.3% - 19.9%. Thus, in any fabricated boron carbide specimen, numerous polymorphic structures can exist. Thus analysis of boron carbide using simulations based on crystal structure becomes extremely challenging. In addition, it suffers from a deleterious deformation mechanism called amorphization under high pressure loads where the crystal structure collapses and the material loses the load bearing capacity and loss of hardness. The present study is a coordinated experimental and computational effort on the mechanical behavior of boron carbide. The pressure dependent response of the amorphized zone and its evolution beneath an indentation are investigated using TEM and Raman spectroscopy. The results are then compared against those under high pressure diamond-anvil cell experiments to understand the pressure dependence of Raman spectra. The consequences of amorphization are addressed with regard to volumetric change in the amorphized material and the stress state in surrounding regions using density functional theory (DFT), density functional perturbation theory (DFPT) and molecular dynamics (MD) simulations. The simulated Raman spectra were compared with experiments to offer insight into the kinetics of amorphization under hydrostatic compression (up to 100 GPa) and homogeneous shear. This analysis has provided new insight into their bonding behavior, Raman spectral characteristics, Hugoniot response and thermodynamics of amorphization process. For the first time, shock simulations are performed to develop pressure-volume relationship (Equation-of-state) and these results have been shown to agree with the vast experimental data already available in the literature. Finally, new avenues are proposed to improve the stability, amorphization resistance, and mechanical performance of boron carbide. Overall, these results provide new insight into the links between polymorph crystal structure, deformation response, and Raman spectra while simultaneously laying the foundation for polymorph-level design of boron carbide. We will rationalize these observations and provide mechanistic arguments towards development of structural ceramics with hardness beyond the of current thresholds.

Keywords: Boron Carbide shock response, Amorphization, Molecular Dynamic Simulations

ABS 149

THE EFFECT OF SUBCRITICAL CRACK GROWTH ON A WEIBULLIAN STRENGTH DISTRIBUTION – THEORY AND EXPERIMENTS

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Subcritical crack growth can change significantly the strength of certain ceramic materials. It will be shown that a generalized strength distribution can be derived analytically in case of a Weibullian inert strength distribution under constant stress rate conditions. A typical method for measuring the parameters of subcritical crack growth is performing constant stress rate experiments in a large range of stress rates. Taking the generalized strength distribution into account for data evaluation, all strength data under different stress rate experiments can be pooled and more accurate data for the strength distribution can be estimated compared to the procedure described in standards. Additionally confidence intervals can be estimated for the crack growth exponent but also for the Weibull parameters of the inert distribution.

Finally a subtle detail is discussed with respect to the measurement of strength of materials which show subcritical crack growth: the influence of the stiffness of testing machines will be demonstrated theoretically and experiments will presented that support these influence.

Keywords: subcritical crack growth, Weibullian distribution

ABS 132

REAL STRUCTURES IN COLLOIDAL PROCESSING USING CONCENTRATED SLURRY

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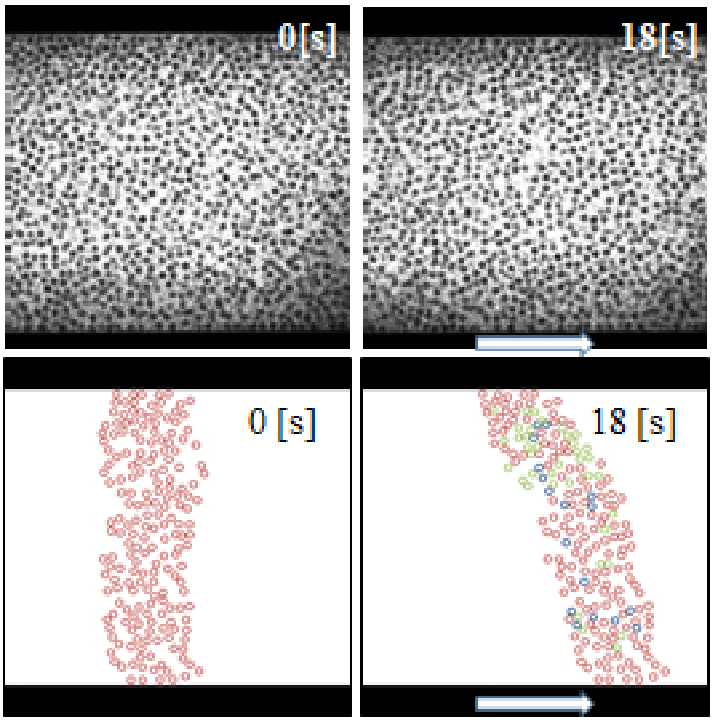
Particles dispersion in concentrated slurry is required for ceramic powder processing. Rheological measurement are usually used for characterization of the slurry such as dispersed or flocculated state. Motions of individual particles in a practical concentrated slurry is difficult to be observed due to opaque liquid. In this study, the internal structure of slurry with high-concentration was directly observed with a confocal laser scanning fluorescent microscope (CLSFM). In experimental, a transparent slurry was prepared by matching refractive index of solution with fine silica particles. The concentration of silica particles was controlled in the range of 30- 50 vol%. In slurry, polyethylene imine was used as a dispersant. When the slurry was passed through a micro flow path under CLSFM, flowing of each particles was observed for a dispersed slurry, whereas cluster of particles with several micrometer was observed for a flocculated slurry. When the shear stress was applied to slurries under CLSFM, particle networks deformed gradually (Fig.1). For the sedimentation test, the cluster consisting of several particles sediment rapidly, whereas fine particles are floating upward direction. The rheological behavior was also measured and related to the observed results.

Keywords: Concentrated slurry, Confocal laser microscope, Colloidal process



ABS 123

APPLICATION OF THE INTEGRATED DIGITAL IMAGE CORRELATION TECHNIQUE ASSOCIATED TO BRAZILIAN DISC TESTS TO IDENTIFY THE CREEP BEHAVIOR OF REFRACTORY MATERIALS

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Refractory materials are well known for their temperature dependent nonlinear behavior. Particularly, at high temperatures, these materials present considerable creep strains, which can limit the lifetime of linings applied to metallurgical vessels. Therefore, viscoplastic constitutive models are often required to simulate the stresses and strains in practical applications. The identification of the mechanical material's parameters poses a major challenge to the refractories industry, specially under tensile loads, and it's frequently expensive and time consuming. In the present study, a new experimental setup based on the Integrated Digital Image Correlation (I-DIC) technique associated with Brazilian disc tests is proposed as an alternative to classic unidimensional tensile and compressive tests. The main advantage of this approach is the possibility to considerably reduce the number of required tests to identify the creep parameters, since in the Brazilian disc specimen the stress field is more complex than in unidimensional tests. The application of this technique has been exemplified through the identification of material's parameters related to different asymmetric creep constitutive models, i.e., models that present different behavior under tensile and compressive stress states.

Keywords: Refractory, Digital Image Correlation, Inverse Identification

ABS 100

GRAIN SIZE DEPENDENCE OF YOUNG'S MODULUS AND THERMAL CONDUCTIVITY

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It is well known that the influence of grain size on the effective Young's modulus is relatively weak, whereas that on thermal conductivity can be comparably large, especially when the crystalline grains have a high intrinsic conductivity. Phase mixture modeling is a popular approach to estimate this grain size dependence. In this approach the grain boundary is considered as a defective or amorphous (glass-like) shell of finite thickness (of order 1 nm) coating the crystalline cores. Thus a single-phase polycrystalline material is considered as a quasi-two-phase composite with a matrix-inclusion microstructure consisting of crystalline inclusions in a matrix of grain boundary phase. Based on an estimate of the boundary property value, the effective property of the material is then calculated via the Wiener-Paul bounds or (in the case of the high phase contrast) the lower Hashin-Shtrikman bound. Results for the different grain shapes are subsequently compared on the basis of equivalent sphere diameters. In the present contribution the predictions of phase mixture models for cubic and tetrakaidecahedral grain shapes are compared with numerical results obtained for these deterministic grain shape models in periodic arrays and for random polyhedral shapes in random arrangement. Digital model microstructures have been computer-generated using the commercial software package GeoDict® (Math2Market, Germany), and numerical calculations have been performed using the same software. It is shown that the agreement between phase mixture models and numerical calculations is excellent for cubic and tetrakaidecahedral grain shape, and that randomly shaped and arranged grains shift the grain size dependence to smaller sizes. The predictions are compared with selected experimental results and literature data for oxide ceramics.

Acknowledgements: Project GA18-17899S, supported by the Czech Science Foundation (GACR).

Keywords: Young's modulus, thermal conductivity, grain size

ABS 82

HYDRODYNAMICS IN MESOSCOPIC SIMULATIONS OF CERAMIC SUSPENSIONS

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The simulations of ceramic suspensions are of great interest to improve colloidal shaping processes. Nevertheless, colloidal suspensions are complex fluids because of the huge length and time scales difference to correctly describe the dynamics of both solid particles and fluid molecules. Several simulation techniques have been developed to address this problem. On the one hand, the solvent may be considered as a continuum medium. This is the case for the basic Brownian dynamics (BD) simulations in which the solvent induces simply friction and random forces on colloids. Therefore, BD simulations are very efficient, but they do not describe hydrodynamic interactions (HIs) between colloids. On the other hand, the solvent may be described by a coarse grained model, i.e. with “solvent particles”. This is the case for the stochastic rotation dynamics-molecular dynamics (SRD-MD) simulation technique, SRD (also called MPCD in the literature, for multi-particle collision dynamics) being a simple particle-based simulation technique of the solvent. Such a simulation technique is able to describe the hydrodynamics of colloidal suspensions much more precisely than BD.

BD and SRD-MD will be first described in detail, especially the SRD parameters tuning the solvent properties, the couplings between solvent dynamics (SRD) and colloid dynamics (MD) and the building of a realistic SRD-MD simulation for a given colloidal suspension. Then, the correctness of the hydrodynamic description in SRD-MD will be illustrated through the slowdown of the colloid diffusion at high colloid concentration. Finally, the importance of taking into account HIs will be discussed for what concerns the aggregation behavior of colloids and in particular the percolation threshold. For that, a comparative study performed with both BD (without HIs) and SRD-MD (including HIs) will be presented.

Keywords: Numerical simulations, colloidal suspensions, hydrodynamic interactions

ABS 31

SIMULTANEOUSLY PROBABILISTIC AND DETERMINISTIC APPROACH (SPADA) FOR DESIGN OF EXPERIMENT: OPTIMIZATION OF THE SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS (SHS) PARAMETERS FOR THE Si-Al-N-O-C CERAMICS

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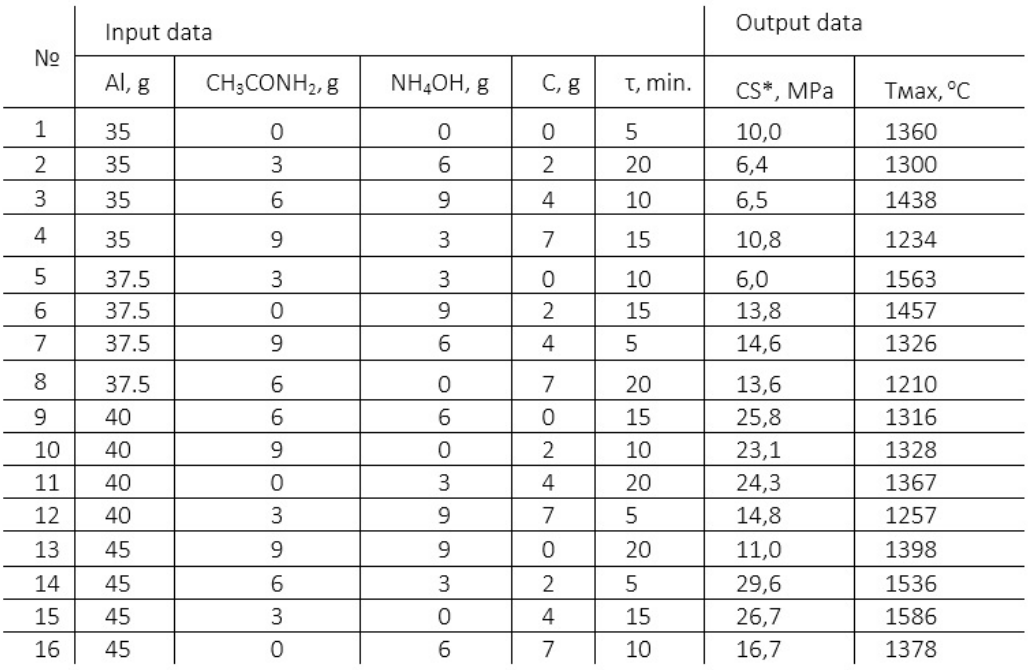
The complexity of the materials on demand is constantly increasing. Multi-component ceramics with the variety of different properties becoming an object of interest. At the same time the experiment optimization algorithm stays unchanged and slows down the further material development process. Majority of the experiments in material science organized in accordance with the classing approach where most of the synthesis parameters stay unchanged and only influence of few parameters gets investigated in a relatively narrow range of possible values. Important step of duplicating of the experiments for statistical data consistency is often neglected. The theoretical calculations of some material properties are often different from each other depending on the chosen database and could be different from experimental data because the complex correlation between the experiment input and output data sometimes stays unknown. Quite often the measured fabrication parameters are completely changing and becoming useless during the scale-up process. The unified approach for the experiment organization could be first step in overcoming some of that challenges. There are many possible ways for the design of experiment (DOE) but none of them got the worldwide popularity in a field of material science. Bio-, medical, social science are the way ahead in integration of the statistics and mathematical approaches to the DOE. Majority of the DOE in material science are based on the direct search or the partial factorial approach. Lack of simple and good examples of integration between the statistical approach, data processing and material science experiment optimization prevents the wide use of other available DOEs. In this work we reintroduce the simultaneously probabilistic and deterministic approach (SPADA) for scientific experiment optimization. The Si-Al-N-O-C ceramic self-propagating high-temperature synthesis (SHS) parameters are used for the method demonstration. Thermokinetic characteristics of the SHS process and compression strength of the final material are studied as a function of charge composition and sample annealing time Table 1. Complex correlation between the batch composition and SHS maximum temperature was evaluated. The simple statistic approach for the DOE which could be easily understood and integrated with any material science experiment is shown. To the best of our knowledge, this method hasn't been reported in English speaking scientific society but have already been mentioned in Russian community. The name SPADA hasn't been ever used before and introduced by the in a first time for the convenience.

Keywords: Design of experiment (DOE),SHS,SPADA

Table 1 Experiment design input and output data



№	Input data					Output data	
	Al, g	CH_3CONH_2, g	NH_4OH, g	C, g	τ, min.	CS*, MPa	Tмах, °C
1	35	0	0	0	5	10,0	1360
2	35	3	6	2	20	6,4	1300
3	35	6	9	4	10	6,5	1438
4	35	9	3	7	15	10,8	1234
5	37.5	3	3	0	10	6,0	1563
6	37.5	0	9	2	15	13,8	1457
7	37.5	9	6	4	5	14,6	1326
8	37.5	6	0	7	20	13,6	1210
9	40	6	6	0	15	25,8	1316
10	40	9	0	2	10	23,1	1328
11	40	0	3	4	20	24,3	1367
12	40	3	9	7	5	14,8	1257
13	45	9	9	0	20	11,0	1398
14	45	6	3	2	5	29,6	1536
15	45	3	0	4	15	26,7	1586
16	45	0	6	7	10	16,7	1378

* CS - compressive strength

S04

ADVANCED STRUCTURAL CERAMICS, COMPOSITES AND REFRACTORIES

INVITED LECTURES

ABS 824

MULTIFUNCTIONAL SILICON NITRIDE/GRAPHENE THICK COATINGS FOR NEW EMERGING APPLICATIONS

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Objective This study is focused on the development of new multifunctional conductive non-oxide multilayered ceramic/graphene thick coatings designed for electrical contacts and switches. The layered sample fabrication is realized using HIP/SPS technologies. Parameters for upscaling are defined simultaneously. Modelling of materials behaviour is done to understand the material behaviour and to identify possibilities for further optimisation and evaluation of functional properties with respect to possible applications, e.g. integrity sensors, ceramics for low cost electrical discharge machining, contacts, switches, electrically and thermally conductive ceramic parts.

Materials & Methods Silicon nitride starting powders together with sintering aids and with different graphene content (0%, 5% and 30%) were dry pressed together and after that the hot isostatic pressing (HIP) was performed to create multilayered ceramic composites. The sintering was performed at 1700°C, 20 MPa nitrogen pressure for 3 hours.
Results
Since the properties of the multilayer coatings are significantly influenced by the interfaces, TEM studies are performed to characterize the interfaces and to provide input for interface engineering. More graphene content decreased the density values. Graphene addition decreased the bending strength, but the 3, 5 and 7 multilayered composites had similar bending strength values. The transition between the 0% and 5% was continuous with a noticeable border, while the 0% layer next to the 30% layer showed exfoliation at some extent after the HIP process.

Conclusions The tailored materials will be applied to energy technology, automotive, aerospace, railway and other transport industries as well as in electronics. The design of the multifunctional conductive non-oxide multilayered ceramic/graphene thick coatings will be adapted according to the requested use-case dependent reliability.

Acknowledgement
The authors thank the support to the FLAG-ERA project „Multifunctional Ceramic/Graphene Thick Coatings for New Emerging Applications”. The authors acknowledge the help in preparation and characterization of composites to: Y. Standke (Fraunhofer IKTS), D. Medved, M. Ivor (IMR SAS) and V. Varga, M. Furkó, and Z. Fogarassy (MTA EK).

Keywords: silicon nitride, graphene, composite

ABS 813

TAILORING MICROSTRUCTURE AND ARCHITECTURE TO DESIGN DAMAGE TOLERANT CERAMICS

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Advanced ceramics incorporate multifunctional design and innovation to produce high-performance applications in the fields of biomedicine, automotive engineering, electronics, energy and mechanical engineering. The combination of ceramics with other materials (metals, polymers or other ceramics) has enabled the fabrication of hybrid systems with exceptional structural and functional properties. However, a critical issue affecting the functionality, lifetime and reliability of these systems is the initiation and uncontrolled propagation of cracks in the brittle ceramic parts, yielding in some cases very high rejection rates of component production.

In this work, design concepts are presented that combine different approaches used in current ceramics engineering to obtain highly reliable ceramic materials with enhanced fracture resistance. The combination of inorganic phases (e.g. alumina) with organic compounds (e.g. PMMA) or metals (e.g. Ni) in a so-called “brick-mortar” composite structure or in a layered architecture, may yield outsatnding toughness values up to 40 MPam1/2 relative to the low toughness of (brittle) bulk alumina (3.5 MPam1/2). However, the high toughness associated with the relatively large deformation upon loading is usually achieved at the expense of the material’s strength (often quoted in the literature as: “conflicts between strength and toughness”). Another research line has focused on ceramic-ceramic composites. It has been demonstrated that tuning the location of “protective” layers within a ceramic multilayer architecture can increase its fracture resistance by five times (from 3.5 to 17 MPam1/2) relative to constituent bulk ceramic layers, while retaining high strength (~500 MPa). The use of tailored residual stresses in embedded layers can act as an effective barrier to the propagation of cracks from surface flaws, providing the material with a minimum design strength, below which no failure occurs. Moreover, by orienting (texturing) the grain structure, similar to the organized microstructure found in natural systems such as nacre, crack propagation can be controlled within the textured ceramic layers. A combination of experiments and modelling is here presented, showing the potential of multi-phase layered architectures in the design of future ceramic components with enhanced damage tolerance. A successful implementation of microstructural features (e.g. texture degree, tailored internal stresses, second phases, interface bonding) in a hierarchical architecture may provide outstanding lifetime and reliability in structural and functional ceramic devices. In this regard, the control of grain boundaries engineered in a layer-by-layer 3D architectural design may hold the key to a new generation of “damage tolerant” ceramics.

Keywords: Textured ceramics, Layered architecture, Damage tolerance

ABS 696

THE PHASE EQUILIBRIUM DIAGRAMS: A KEY TOOL FOR CERAMIC MATERIALS SCIENCE

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Advanced structural ceramics, composites and refractories are complex materials able to withstand extreme working conditions -i.e. high temperatures in contact with higly corrosive liquids and/or atmospheres. The potential mass transport associated with the high temperatures imply that equilibrium of the system is frequently attained during service, at least at local scale. This characteristic allows the basic principles of phase equilibrium diagrams to be used in this field of science and technology.

Equilibrium diagrams are valid, not only for predicting the final equilibrium state, but also to infer the path through which the changes towards equilibrium take place. In this context, equilibrium diagrams are a key tool in materials science.

Our research team (Group of Phase Equilibrium Diagrams, http://www.icv.csic.es/en/node/121) has 40 years' experience in the experimental and theoretical study of complex phase equilibria diagrams in the field of ceramics.

In this talk, the main criteria for the use of phase equilibrium diagrams is discussed. The microstructural design for improved refractories and advanced structural ceramics, as well as, the response of these materials in use are addressed. Appropriate examples in different systems will be discussed.

Keywords: Phase equilibrium diagrams, Refractories, Corrosion

ABS 657

EFFECT OF TRANSITION METAL ADDITIVES ON THE STRUCTURE AND PROPERTIES OF ZIRCONIUM DIBORIDE CERAMICS

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The objective of this presentation is to describe the effect of transition metal additives on the microstructure development and properties of zirconium diboride ceramics.
Fully dense ZrB2 ceramics containing Ta additions up to 6 at% were prepared by reactive hot pressing. Starting materials were hydrides of Zr and Ta along with amorphous boron. Powders were mixed by ball milling and then densified at 2100*C.
Previous studies have noted the formation of core-shell morphologies when transition metal silicides such as MoSi2 or TaSi2 were added to ZrB2. The core is nominally pure ZrB2 while the shell is a solid solution in which transition metal atoms substitute onto Zr sites in the lattice. The shells grow by diffusive transport of material during densification. The effect of these solid solution additions on microstructure development and properties of ZrB2 ceramics was examined in the present study. Analysis by x-ray diffraction and scanning electron microscopy with energy dispersive spectroscopy indicated that Ta formed a solid solution with the ZrB2 and did not form a second phase. Further analysis by atom probe tomography confirmed the uniform distribution of Ta in ZrB2 grains. The effects of transition metal additions on thermal and mechanical properties have also been studied. Thermal conductivity decreased for addition of any transition metal species to ZrB2. Likewise, transition metal additions changed the fracture behavior and mechanical properties.
Transition metal additives decrease thermal conductivity of zirconium diboride due to increased phonon and electron scattering. In addition, transition metal additives alter both the fracture behavior and mechanical properties of zirconium diboride ceramics.

Keywords: zirconium diboride, thermal conductivity, strength

ABS 613

STABLE FRACTURE OF CERAMIC INTERFACES AT THE MICRON SCALE

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The fracture toughness of ceramics is often dominated by the structure of their grain boundaries. Our capacity to improve the performance of ceramic components depends on our ability to investigate the properties of individual grain boundaries. To measure the fracture energy of individual interfaces we have used a double cantilever geometry to obtain stable crack growth and we calculate the fracture energy under a constant wedging displacement. Our tests have proved it is possible to initiate and stably grow a crack in a controlled manner in ceramic materials for several microns. This approach has been validated on SiC where it gives a good approximation of the surface energy and then extended to SiC bi-crystals along with Ni-Al2O3 interfaces where crack blunting and bridging mechanism can be observed and measured. Finally we will show the effect of moisture on the fracture energy of an individual oxide interface.

Keywords: Fracture, Micron Scale

ABS 509

DEVELOPMENT OF ELECTRIC DISCHARGE MACHINABLE ZTA CERAMICS WITH ENHANCED MACHINABILITY AND MECHANICAL PROPERTIES

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Customized manufacturing of complex shape structural ceramic components in small lot sizes by the conventional process route is very costly due to the final hard machining operations. The problem is today widely addressed by novel additive manufacturing technologies which are - at least to date - unable to produce components within in geometrical tolerances and surface qualities that are acceptable for mechanical engineering applications. Electrical discharge machining, a non-conventional machining technology has been widely applied in machining of complex metal and cemented carbide components. The technology can be applied for machining of ceramics as soon as the workpieces are sufficiently conductive. Electrical conductivity is introduced by adding a percolating dispersion of a transition metal carbide, boride or nitride. ED-machinable ceramics with a zirconia toughened alumina matrix are extremely interesting for applications requiring high hardness and abrasion resistance together with thermomechanical compatibility in connection with steel such as in tools, mold inserts and dies.

The feasibility of the concept was proven in 2013. After that the development of ED-machinable ZTA has focused on simultaneously improving machinability, i.e. material removal rate/cutting speed achievable surface quality and machining accuracy and mechanical properties such as hardness, strength and toughness.

For this purpose in detail studies varying the type, grain size and volume fraction of the electrically conductive phase and the composition of the ZTA matrix were performed. In a holistic approach the subsequent stages of the processing cycle, powder technology and feedstock preparation as well as the pressure assisted sintering by SPS and HP were addressed. Machining tests to elucidate the EDM characteristics depending on the compositional parameters were carried out. With the latest generation of ZTA-TiC and ZTA-NbC composite ceramics improvements in strength of more than 20% compared to the initial recipes are possible. At the same time machining speed and surface quality was improved and a reliable scale-up process for feedstock preparation was elaborated.

Keywords: mechanical properties, electric discharge machining, ZTA

ABS 485

SOME ISSUES ON MANUFACTURING OF NONOXIDE FIBER REINFORCED NONOXIDE CERAMICS

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Nonoxide fiber reinforced composites are promising candidates for high temperature applications under severe conditions. In inert atmosphere they can play their role as creep resistant composites in an unbeatable manner. However under oxidative atmosphere the long term stability may be limited due to oxidation and succeeding degradation of the mechanical properties. Then environmental barrier coatings as well as self healing effects in the bulk material are necessary in order to keep the properties of these materials on a sufficient level for long term application in e.g. gas turbine engines. For aero-engines the industry strongly focusses on SiC/SiC composites and some parts, e.g. shrouds, are already in serial production.

In order to manufacture such high performance SiC/SiC composites first of all the fibers must be protected against any degradation due to infiltration process of the matrix. Therefore a chemical stable fiber coating is mandatory. From the todays viewpoint CVD coating systems with multiple layers seem to be the most promising approach even if there are severe attempts to introduce dipcoating techniques as an alternative method. Typically a BN layer is applied for adjustment of the mechanical bonding between fiber and matrix. This layer allows fiber bridging during loading without brittle failure. An additional SiC layer protects the fiber against corrosive attack during manufacturing and during use and an optional final coating optimizes the adhesion of the matrix being infiltrated in the following processing step. Once the fibers are coated homogeneously then the matrix may be impregnated. Here CVI techniques as well as polymer infiltration and pyrolysis PIP and even liquid silicon infiltration LSI are potential methods. They all have certain advantages and drawbacks which will be discussed. The main goal is to achieve a dense matrix as then possible oxidation and corrosion attack may be reduced as diffusion pathways are minimized. Therefore combinations of these methods are favorable in order to maintain most efficiently a dense and longterm stable matrix. Finally a fully functional coating system with multiple layer system must be applied on the surface. Whereas the chemical systems are well developed there are still adhesion issues to be solved in order to prevent spallation during use.

The presentation focuses on these various manufacturing issues of nonoxide composites and discusses the challenges in material development.

Keywords: Nonoxide CMC,LSI,PIP

ABS 473

SHORT-FIBER CMCs

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Ceramic Matrix Composites (CMCs) are increasingly used in non-space applications like combustion environment, metallurgy, gas turbines and friction elements (brake disks and pads). Typically, these materials are reinforced with a continuous 2D fiber architecture and are still very expensive. Short fiber reinforced composites (SF-CMCs) have some beneficial properties compared to continuously reinforced ceramics like in-plane isotropic mechanical as well as physical properties and show the possibility of a near net-shape manufacture. Short fiber CMCs offer a high potential of cost efficiency as cutting losses during the processing can be minimized and cheaper fibers are applicable. In this paper two novel approaches to fabricate SF-CMCs by use of chopped fibers are presented. One approach describes a non-oxide material C/SiC, based on short carbon fibers and a PEEK matrix as a thermoplastic precursor, manufactured via the LSI-process. The other development describes an all oxide fiber composite (OFC), based on short alumina fibers and an Al2O3/ZrO2 matrix, manufactured by a fiber spraying process. For both SF-CMCs, flexure strengths in the range of 100 MPa and strain levels up to 0.5% can be achieved, sufficiently high for different applications. As the critical fiber length is much higher in comparison for example with CFRPs, investigations have been conducted in terms of fiber lengths, fiber deposition methods as well as suitable test procedure. Results about the processing-microstructure-properties relationships of both SF-CMC materials are discussed.

Keywords: Short fiber reinforcement, CMC, Fiber length

ABS 309

LOW CARBON AND ZERO CARBON BRICKS FOR ULTRA LOW CARBON STEEL PRODUCTION THROUGHOUT INNOVATIVE BINDER SYSTEM

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To meet an increasing demand for cold rolled steel sheets of improved mechanical properties, and to cope with the change of annealing process from batch-type to continuous, it is necessary to establish a technique for making ultra-low carbon steel with carbon concentration lower than 20ppm in the steelmaking process. Ultra-low carbon steel is used widely for automotive industry. Attending this demand requires refractory materials for the steel ladle with minimum or zero carbon content.

MgO-C is the typical refractory used for the slag line for the steel ladle. No significant changes have been introduced in the refractory binder system since the development of tempered MgO-C bricks in the 80´s decade. Several sources of pitch compounds and novolac and resol phenolic resins are applied as binders for most of the types of carbon containing refractories. At 2000's, a new carbon binder was designed from the blend of powder pitch and the resins providing bricks of excellent performance in a wide temperature range. Next generation of tempered MgO-C bricks is based on a new binder system that allows a reduction in the final carbon content over 50% with no damage in corrosion and thermomecanical properties.

Usually, the current refractory solution for metal lining for steel ladle for ultra-low carbon steel production is a fired brick. Also a tempered Alumina-Magnesia brick was developed as a technological alternative with a zero carbon binder. Spinel $MgO.Al2O3$ formation during ladle operation allows to an expansive reaction that can prevent metal and slag infiltration, better corrosion resistance and confident operational safety.

This work presents the development of the ultra-low and zero carbon bricks for steel ladle with an innovative and environmental friendly binder technology. Properties and customers' performance compared to traditional products are highlighted.

Keywords: refractory, steel ladle, binder

ABS 244

FROM MULTIFUNCTIONAL POWDERS TO HIGH-END CERAMIC PRODUCTS

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The development of a product based on a novel ceramic composite consists on different phases: powder synthesis and conditioning, shaping, sintering and finishing. The control of each one of these processes is of vital importance in order to obtain a reliable product. The present work will deal with the experiences of the company Nanoker Research S.L. in the development of different high-end products based on ceramic composites for the industry in the last years. A special emphasis will be put on the synthesis and conditioning of nanostructured powders and in the consolidation of these powders by pressure-assisted sintering technologies. Several examples of products developed for the industry (aerospace, particle accelerators, solar) will be addressed. Different ceramic composite materials will be covered in the present work: UHTCMC´s (Ultra high temperature ceramic matrix composite), graphite metal carbide composites and ceramic-metal composites (cermets).

Keywords: UHTCMC, Pressure assisted sintering, Cermet

ABS 217

ULTRA-HIGH CREEP RESISTANT SILICON CARBIDE CERAMICS

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Freeze-granulated and afterwards under infrared lamp annealed silicon carbide powder was densified to the full density without any sintering aids by hot-pressing/ultra-rapid hot-pressing at 1850 °C. This densification temperature is at least 150-200 °C lower compared to the up to now known solid state sintered silicon carbide powders. Presented silicon carbide hot-pressed ceramics have excellent mechanical properties. Samples densified by ultra-rapid hot-pressing have also full density and hardness of 27.4 GPa. Partial phase transformation beta/alpha - SiC was observed in the granulated and hot-pressed/ultra-rapid hot-pressed samples.

The oxidation behavior of this way prepared SiC ceramics at 1350-1450°C/0-204h was investigated This way prepared SiC ceramics is characterized by an excellent oxidation resistance (4.91x10-5 mg2/cm4h at 1450°C).

Creep rate of ultra-rapid hot-pressed samples at 1450 °C and 100 MPa load in 4-point bending test is 3.8 x 10-9 s-1 and at 1400 °C and the same load conditions is 9.9 x 10-10 s-1.

Creep rate of the same at load of 400 MPa and temperature of 1750 °C at a comprersion mode was only 10-7 s-1. This is the lowest creep rate of SiC at such conditions found in the literature. Enhanced beta/alpha SiC phase transformation was observed after the creep test.

Keywords: silicon carbide, oxidation resistance, creep resistance

ABS 173

MODERN REFRACTORIES: ADVANCED CERAMICS? THEY CERTAINLY ARE

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Refractories are unique ceramic materials used in linings of vessels to contain and process fluids at high temperatures. They can sustain complex combinations of thermomechanical stresses and chemical/ physical wear generated by fluids and chemical agents used during process. Being materials able to sustain operation conditions at temperatures typically above 1000°C, refractories are identified as advanced ceramics. Nevertheless refractory materials were, in recent days, often associated to traditional old well-known materials mainly applied in heavy declining industries (for steel, cement and glass making... etc.). Likewise refractories education had an image problem. Refractories engineering has been considered as a technical specialism rather than a scientific subject [1]. This negative image was the main reason which led to high difficulties in recruiting high potential students in the field of refractory materials [2]. Sometimes the term “refractory” is not used any more in titles, keywords of articles or even in names of institute divisions.
To overcome this situation, FIRE (The Federation for International Refractory Research and Education) aimed at implementing a new training methodology based on a relevant interconnections between the main experts within academic poles within the world. The paper will both illustrate some of the ongoing cooperative programmes in the field of refractories research and at the same time it will show what beautiful complex high tech materials refractories are.

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[2] Huger, M. ‘Education on Refractories in Europe’, UNITECR 2017, proceedings 040.

Keywords: Refractories Research, Collaboration, Education

ABS 137

MULTI-SCALE THERMAL PROTECTIVE SYSTEMS FOR EXTREME ENVIRONMENTS: DESIGN, PROCESSING, PROPERTIES AND MODELING

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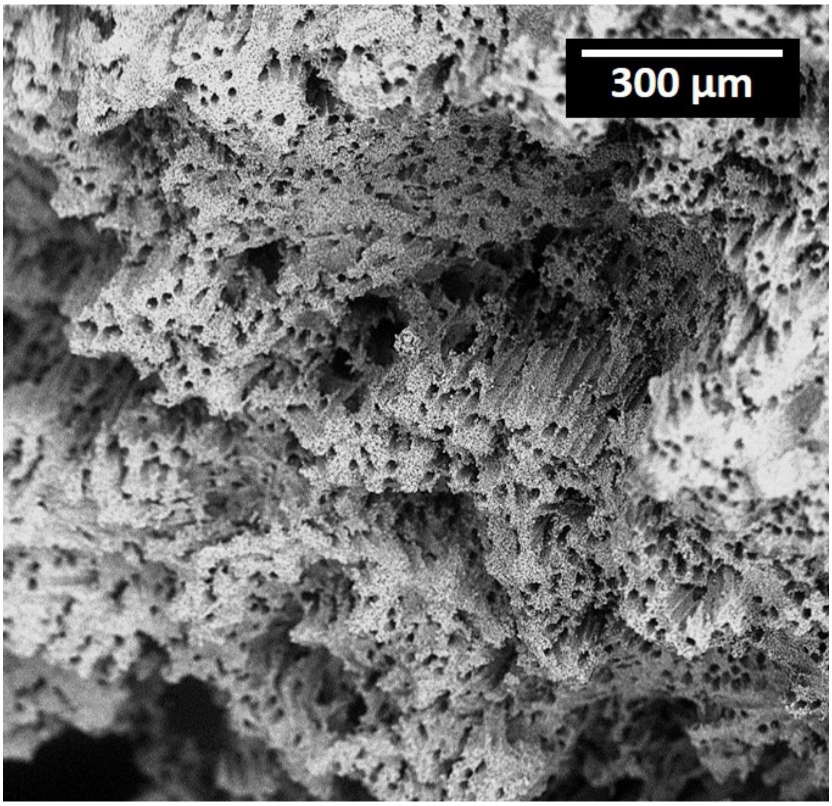
Thermal protective systems for hypersonic vehicles can provide additional strategies to survive the severe conditions they endure: large heat fluxes, extreme temperatures, extensive thermal gradients, stagnation pressures and oxidative environments. These elements also need to show minimal material ablation, overall weight, while meeting complex shapes and tolerances for integration with other aircraft components. Multi-scale porous UHTCs with a suitable combination of microstructure (pore size, type and amount) and properties (thermal conductivity, pore network connectivity and thermomechanical response) may meet those requirements. However, deciding what that suitable combination of microstructure-properties is the real challenge.

In this work, a dual approach for design and manufacturing of multi-scale porous UHTCs is presented. Highly aligned porous channels are produced in titanium diboride using electrospun fibers as sacrificial fillers, with a multi-scale porosity between 50 and 80%, with controlled alignment to direct the flow of a second phase or divert the heat away by tailoring thermal conductivity. The microstructure and thermal and mechanical properties are characterized along and across the pores axis, and compare with analytical models. The results show that the manipulation of the highly aligned porous microstructure allow to control the thermal and mechanical properties as a function of the direction of the pores. Computational approaches are validated by experimental characterization of actual samples, as a pathway to develop predictive capabilities. This integrated combination of predictive modelling of porous UHTCs with tailored processing routes to create porous structures is key to match the desired performance.

Keywords: multi-scale, porous,UHTC



ABS 62

MATERIAL INFORMATICS ACCELERATES INNOVATIVE DESIGN OF MULTIFUNCTIONAL THERMAL ENVIRONMENTAL BARRIER COATING MATERIALS

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SiCf/SiC ceramic matrix composites (CMCs) are the key high temperature structural materials in future gas turbine engines. Multifunctional thermal environmental barrier coating (TEBC) is critically requested to protect CMC-components from severe high temperature oxidation and corrosion in extreme combustion environments. There are crucial challenges for the optimal choices of TEBC candidates due to their complex crystal chemistry and tunable performances. Highly efficient screening of advanced TEBC materials would be promoted based on material informatics of diverse candidates. Strategic material-genome initiative would also prevail to disclose mechanisms of property diversity and to further adopt novel concepts for the design of robust TEBC for advanced SiCf/SiC CMCs.

Keywords: Environmental Barrier Coating, Design and Optimization

ABS 7

DISCOVERY OF NEW MAB PHASE AND 2D NANOSHEETS MABENE IN Cr-Al-B SYSTEM

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MAB phases, wherein M is a transition metal, A is Al or Si, and B is boron, are appealing due to the unique properties that they display. From structure point of view, they have layered crystal structure and anisotropic chemical bonding; from property point of view, they exhibit good electrical and thermal conductivities, moderate modulus, being resistant to thermal shock and oxidation, and tolerant to damage like MAX phases. The combination of these properties makes them promising for high and ultra-high temperature applications. Up to now, the theoretically and experimentally studied MAB phase include (CrB2)nCrAl (n=1, 2, 3), W(Mo)AlB, M5Si3B, Y5Si2B8 and YAlB4. Among them, compounds in Cr-Al-B system can be described as alternating stacking of (CrB2)n and CrAl layers along a specific crystallographic direction. Recently, a new compound Cr4AlB4, which is formed by alternatively stacking of (CrB)2 layer and Al layer, was discovered by the authors' group. In this presentation, the process for the discovery of this new MAB phase and its crystal structure, electronic structure and elastic and thermodynamic properties will be introduced. The discovery and characteristics of the 2D CrB called MABene prepared from Cr2AlB2 will also be presented.

Keywords: MAB phase, MABene, New compounds

S04

ADVANCED STRUCTURAL CERAMICS, COMPOSITES AND REFRACTORIES

ORAL PRESENTATIONS

ABS 858

DIFFUSION OF CARBON IN TUNGSTEN-CARBON SYSTEM

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Harnessing clean energy from nuclear fusion is one of the humanity's most ambitious goals and our ticket to a more green, sustainable and energy sufficient future. One of the main difficulties of designing of the fusion reactor is the development of suitable plasma-facing materials that could sustain high temperatures, thermal fluxes, gas retention and neutron embrittlement, while retaining acceptable mechanical properties. Taking into account all those limitation, tungsten is still considered a primary candidate for the divertor material in DEMO fusion power plant, along with other W-based composites. Pure tungsten was a solid choice for the divertor in ITER since the operating temperature will be around 400 °C so brittle-to-ductile transition and recrystallisation were not of great concern. However, working temperatures in the future DEMO reactor will be higher than 1000 °C, with spikes up to 1600 °C which calls for a better performing material. Our group at JSI developed a W-WC composite with improved mechanical and thermal properties, but the additional carbon in the system presented a different sent of challenges. To better understand the interactions in the system, we prepared a functionally graded composite based on W-WC. We have shown that graded/layered W-WC composites are indeed possible to manufacture by the spark plasma sintering (SPS). Thorough phase composition (XRD) and microstructure analysis (SEM and EBSD) we obtained valuable information about phase gradient and the orientation of grain in the composite.

Keywords: fusion, tungsten, tungsten carbide

ABS 853

PROCESSING AND OXIDATIVE STABILITY ZIRCONIUM DIBORIDE BASED ULTRA HIGH TEMPERATURE CERAMICS

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The effects of AlN substitution on sintering, oxidation and thermal properties of ZrB2-SiC are investigated. Up to 10 vol% AlN was substituted into ZrB2-30 vol% SiC by replacing an equivalent amount of ZrB2 or SiC. Samples were all sintered to nearly full density (93.5%~99.4% depending on compositions) by pressureless sintering. AlN substitutions limited the grain growth of ZrB2. Oxidation resistance of the composites were tested at several temperatures up to 2000 °C both static and cyclic oxidation tests. AlN substitutions affected the oxidation behavior by formation of Al2O3 and/or aluminosilicates. X-ray photoelectron spectroscopy (XPS) showed the presence of Al2O3 and SiO2 on the surface. Presence of Al2O3 which could possibly lead to a modification in the viscosity of the glassy oxide scale as well as increased the viscosity of SiO2 scale at a higher temperature (1600 °C). Replacement of ZrB2 by AlN resulted in a more protective scale both at 1000°C and 1600°C. Substitution of SiC by AlN resulted in a compromise of the oxidation behavior at 1600°C due to devitrification of the scale. Several samples were also cycled between 2000C and room temperature with plasma heating in a 100 torr air pressure (21% oxygen). Volatility and vapor pressure diagrams were constructed to assess the thermal stability of the oxides formed. A delicate balance in ZrB2, SiC and AlN is required for optimal performance.

Keywords: UHTC, High Temperature ceramics, Oxidation Resistance

ABS 825

REACTION OF REFRACTORY CARBIDES WITH IRIDIUM AS A NEW SOURCE FOR FORMATION OF THE ULTRA-HIGH TEMPERATURE MATERIALS

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Progress in aerospace is related to the development and modernization of propulsion systems capable of operating under extreme environmental conditions. There are several concepts to protect the structures from degradation at temperatures above 2000 C. These concepts are based (i) on the ability of some systems to self-healing, e.g. HfB2-SiC system; (ii) usage of so-called high-entropy ceramics, effectively preventing diffusion of oxygen inwards the material; (iii) usage of the materials that have an exceptionally low recession rate in oxygen, such as multilayered iridium coatings. However, these concepts have disadvantages. There is an urgent need to develop new approaches to the design of ultra-high temperature materials.

The concept proposed by us is based on the usage of iridium-containing compounds - iridides of refractory metals - as the base elements of ultra-high temperature materials. It was stated that the liquid phase formed at the eutectic melting of the multicomponent system (iridium in combination with carbides, borides and some other refractory compounds) initiates the interaction of its components, which result in the formation of refractory iridium-containing compounds with a melting point higher than the temperature of the eutectic formation. Such approach allows in situ to obtain in one-stage gas-impermeable materials and coatings. The fundamental problems in the series the mechanism of formation of iridium-based intermetallics from refractory carbides and iridium – microstructural and functional properties - response of the iridium-based materials on the extreme impact of temperature and aggressive environment will be discussed.

The work was supported by Russian Science Foundation #18-19-00075

Keywords: refractory carbides, iridium, ablation

ABS 821

POROUS MULLITE-BASED CERAMICS FABRICATED BY FOAM CASTING

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Nowadays the investigation on the structure, behavior and properties of mullite foams is strongly motivated by industrial demands for high-temperature applications. The preparation and stabilization of kaolinite-based foams are discussed within this work. The foaming procedure is based on the mixture of pre-prepared air/surfactant sacrifice fugitive and kaolin slurry stabilized by surfactant and hydrating additive. Demoulded samples were dried and sintered to mullite-based material. Prepared foams were studied as a possible refractory lining with sufficient thermal stability, porosity, thermal conductivity and mechanical properties. Porous samples of the walls thickness within the nanometers scale can be prepared by this method. Therefore high-temperature behavior, bulk, thermal and mechanical properties of obtained foamed products by means of high temperature X-ray diffraction analysis, thermal and porosity analysis and scanning electron microscopy were studied.

Keywords: mullite foam ceramics, microstructure, refractory

ABS 820

THE MACHINABILITY STUDY OF BONE ASH CONTAINING CERAMIC

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A ceramic based on the mixture of calcined animal bone ash, kaolen and NaF has been formulated to investigate its potential to be used as machinable ceramic. The ceramic was prepared in granulated form after being mixed/milled in ethanol for 24 hours. The granules were dry pressed in purposefully shaped steel dies to prepare cylindrical pellet and rectengular bar shaped specimens for carrying out sintering and mechanical behavior studies. The specimens were sintered at 800, 950 and 1000°C for 2 hours. The sintered specimens were characterised by measuring bulk density, water absorption, firing shrinkage, micro hardness, elastic modulus, flexural strength. The crystalline phases developed in the microstructure of sintered specimens were identified by XRD. The microstructure was also analyzed by SEM and EDS studies.

It was found that the densification level increased with the increase of sintering temperature. Typical elastic modulus and flexural strength values for the samples being sintered at 1000°C were, 37 GPa and 12 MPa, respectively. These relatively low elastic modulus and flexural strength values was due to highly porous microstructure as microstructural analysis revealed. The identified crystalline phases are hydroxyapatite, flourapatite and nepheline for all sintering temperatures. Only the sample sintered at 800°C had additional fluorite crystals. Vickers Hardness Values (HV) were measured to characterize the sintered specimens's suitability for machining. The calculated brittleness index values of sintered samples were less than 4.3 mm½ which indicate good degree of machinability. Drilling tests also verified their suitability for machining. The calculated machinability parameter (m) for all the samples sintered at different temperatures had positive values indicating good degree of machinability. However, the samples sintered at 800°C showed the best drilling depth without any fracture. It was found that machinability parameter and drilling test results support each other.

Keywords: Machinability, Bone Ash, Characterization

ABS 717

CONTROL OF ALUMINIUM TITANATE CONTENT IN CERAMICS OF THE Al_2O_3-TiO_2 SYSTEM

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Thermally sprayed coatings of the Al2O3-TiO2 system containing 3, 13 and 40 mass-% TiO2 are used for more than fifty years in a big variety of tribological, mechanical, electrical, corrosive, and high-temperature applications. In addition to their unique properties, materials of this system are environmentally friendly and cost-efficient, as both aluminium and titanium are aboundingly found in the earth crust. However, depending on the technology of feedstock powder preparation and on the spray process conditions a number of so far uncontrolled changes in the chemical and phase composition occur. These changes a mostly related to the formation and stability of aluminium titanate (Al2TiO5) in feedstock powders and thermal sprayed coatings. In order to understand these processes for new developments in the field of oxide coatings, several experimental series were carried out and the results are presented in this contribution. The influence of MgO additions and starting powder properties (Al2TiO5, Al2O3 + TiO2) on phase formation. Two preparation routes with a total of 4, 8, 44, 56, 90 mass-% TiO2 are applied: sintering of presynthesized Al2TiO5 powders in a two-stage process (Al2TiO5 powder synthesis, sintering) and the reactive sintering of Al2O3 and TiO2. Microstructure, sintering behavior and mechanical properties are investigated.

With MgO addition the reaction rate and temperature of Al2O3 and TiO2 under the formation of solid solution Al2(1-x)MgxTi(1+x)O5 is enhanced. Additionally, stabilization test of Al2TiO5 and Al2(1-x)MgxTi(1+x)O5 at different temperatures (800 - 1200 °C) for 100h reveals a shift to higher decomposition temperature for MgO stabilized Al2TiO5.

Keywords: aluminium titanite,Al2O3-Al2TiO5-TiO2 composites,Al2TiO5 ceramics

ABS 794

THE EFFECT OF ADDITIVES DURING THE SPARK PLASMA SINTERING OF ALUMINA-BASED CERAMICS

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Objective Alumina is one of the promising ceramic materials for a wide range of structural applications due to the combination of its high hardness, heat, and chemical resistance. These properties of alumina can be used only with a fine-grained structure of this ceramic.

There are two effective methods for obtaining a fine-grained structure in alumina-based ceramics: application of additives and Spark Plasma Sintering (SPS) method.

There are a lot of articles about SPS of alumina ceramics, but none of them provides a thorough analysis of the sintering kinetics of each of the stages of the sintering process and the investigation of the role of the additives at each of these stages.

It's well known, that small differences in starting powders and sintering conditions make the comparison of experimental results carried out at different laboratories dubious. That's why the investigation of each sintering stage carried out in one laboratory seems promising.

Materials and methods The starting material used in this study was an Al2O3 powder (d = 0.2 μm) and its mixtures with 0.5%vol. of MgO (d ~ 0,1 μm), TiO2 (d < 0.5 μm) and ZrO2 (d = 0,03 μm). Sintering was carried out using the «DR. SINTER SPS-625» (SPS SYNTEX INC. Ltd., Japan). The activation energies of shrinkage for all stages were determined.

Results Shrinkage behavior of alumina can be described as a sequence of initial, intermediate and final sintering stages.

It was shown that the additives do not change the kinetics of shrinkage at the initial and intermediate stages.

Densification at the initial stage is controlled by grain boundary diffusion of alumina (340 kJ/mol).

Rapid densification at the intermediate stage is caused by plastic deformation, which is controlled by bulk diffusion (power creep law). The activation energy at the intermediate stage was estimated at 530 kJ/mol.

Grain growth at the final stage is controlled by grain boundary diffusion and depends on the difference in the way of their interaction with alumina: Zener effect for ZrO2 or drug solution for MgO and TiO2.

Conclusion The effect of additions of 0.5%vol. of MgO, ZrO2 or TiO2 was observed only at the final stage of SPS of alumina.

Keywords: ceramics, alumina, spark plasma sintering

ABS 757

HARDNESS AND FRACTURE TOUGHNESS OF ALUMINA AND ZIRCONIA COMPOSITES WITH DIFFERENT AMOUNTS OF REDUCED GRAPHENE-OXIDE SINTERED BY SPARK PLASMA SINTERING

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Objectives The main goal of this study is the analysis of the mechanical enhancement of hardness and fracture toughness in reduced graphene-oxide (rGO) reinforced alumina and zirconia ceramics, and to compare the results with those found in the same ceramics without this secondary phase.

Materials and methods The materials studied have been: Al2O3, Al2O3 + 2 vol.% rGO, Al2O3 + 6.7 vol.% rGO and ZrO2, ZrO2 + 2 vol.% rGO, ZrO2 + 6.7 vol.% rGO, ZrO2 +7 vol.% rGO.
All the materials have been sintered by spark plasma sintering at 1300 °C, previously, colloidal processing have been performed in order to optimize the distribution of the secondary phase in the ceramic matrix.
Raman spectroscopy was carried out in order to study the integrity of reduced graphene-oxide (rGO) before and after sintering. The microstructure of the samples was examined by high-resolution scanning electron microscopy (HRSEM).
The hardness and fracture toughness of the specimens were measured by means of the indentation technique with a conventional diamond pyramid indenter.

Results Homogeneous dispersions of the powders have been obtained. The integrity of the rGO in these composites was proved. For zirconia composites, in all the cases the average grain size was constant and equal to ~ (0.2-0.3) μm. For alumina composites, the average grain size was between ~ (0.5-1.0) μm.
All the composites of zirconia and alumina exhibited systematically lower values of hardness compared to the values of pure materials. The fracture toughness of the composites was the same of the monolithic materials within experimental uncertainty.

Conclusions Homogeneous mixtures of alumina and zirconia with rGO have been obtained from concentrated aqueous suspensions after rheological optimization and subsequent freeze drying. Fully-dense Al2O3 + rGO and ZrO2 + rGO composites have been fabricated by SPS.
The analysis of the room-temperature hardness and fracture toughness allows conclude that rGO gives rise to a similar mechanical response.

Acknowledgements
The acknowledge the financial support awarded by the Regional project of Excellence of “Junta de Andalucía” P12-FQM-1079 and the Spanish MINECO and FEDER funds through the projects MAT2015-71411-R and MAT2015-67586-C3-2-R.

Keywords: Zirconia, Hardness, fracture toughness, Reduced Graphene Oxide

ABS 755

FABRICATION OF SiC CERAMIC MATRIX COMPOSITE BASED ON ADDITIVE MANUFACTURE AND GEL-CASTING

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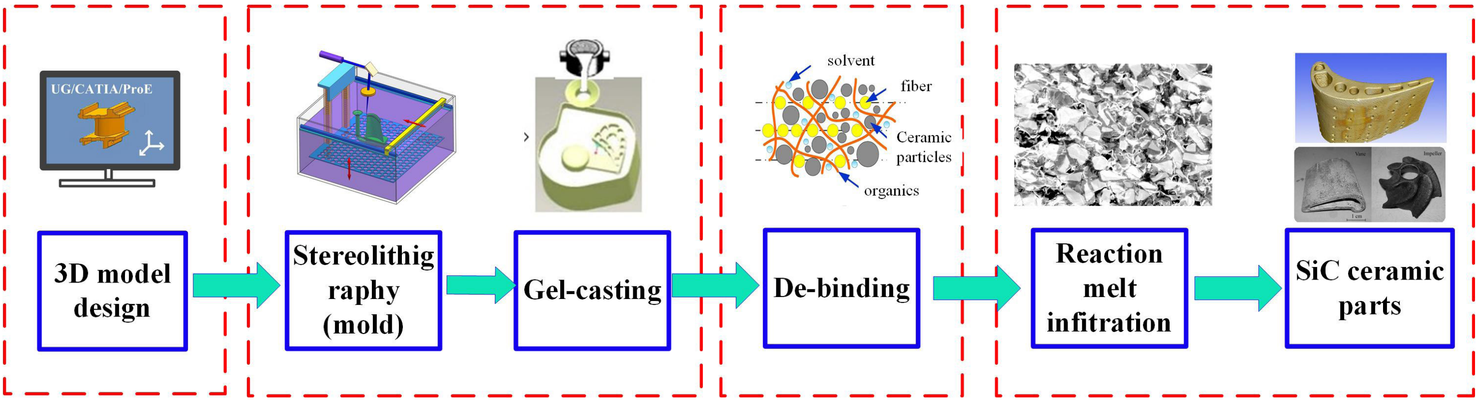
Due to its low density and excellent high temperature performance, SiC ceramic matrix composites have become the candidate materials for aerospace hot end components. However, it is difficult-to-machine material for its high hardness and good wear resistance. Based on additive manufacturing, gel-casting and reaction melt infiltration (RMI) technology, we put forward a method to fabricate Cf/SiC composites part. The residual silicon in the matrix has detrimental effects on high-temperature mechanical properties of SiC ceramic matrix composites, limiting wide application of the material in high-temperature oxidation environment. Therefore, the research of residual silicon control is of great significance.

The influences of particle size distribution and dispersant on the viscosity of ceramic slurry was studied, and the optimal proportion of particle size and the optimum content of dispersant were determined. By the simulation of the ceramic slurry filling process, we found there would be more pores formed in the green by gel casting if viscosity rises. When the viscosity of the slurry was 1.2Pa·s, the simulation results showed that the residual air volume was 2.8vol%; with the increase of the viscosity of the slurry further, the residual air volume also increased rapidly. Therefore, the upper limit of slurry viscosity was 1.2Pa·s.

The influence of the composition of the green on the residual silicon content of SiC ceramic matrix composites was studied. The carbon content in the green was increased by adding carbon black or short carbon fiber in the ceramic slurry to reduce the residual silicon content in the sintered . The results showed that the content of residual silicon decreased first and then increased with the carbon black addition. When the carbon black content was 6wt.%, the residual silicon content reached its the lowest value (33.4vol%). The residual silicon content decreased with the increase of short carbon fiber addition. When the content of short carbon fiber was 18wt.%, the residual silicon content reached its the lowest value (26.8vol%), and the bending strength of the sintered was 343±19 MPa at 1350°C. The influence of residual silicon content on the bending strength of SiC ceramic matrix composites was studied. It was found that the decrease of residual silicon content could improve the bending strength.

Keywords: gel-casting, additive manufacturing, SiC ceramic matrix composite



ABS 739

MULLITE PHASE FORMATION AND REACTION WITH TUNGSTEN TRIOXIDE AS CATALYZER

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Mullite is synthesized by solid-state reaction process, using silicon and boehmite as raw materials and tungsten trioxide as catalyst. The effect of WO3 on mullite reaction at 1100 oC and 1200oC is investigated. For demonstration the phase development, samples were directly quenched in water after calcination, electron probe X-ray microanalysis was used to measure the phase changes and compositions of the phases. XRD results show that with addition of WO3, tungsten rich oxide compound, Al2W3O12 formed in system, and lead to a decrease of about 200 oC in the initial mullitization reaction. The experimental results of quenched samples show that WO3 assisted catalytic mechanism are based on dissolution-precipitation process. The [WO4] clusters in Al2W3O12 is proposed to be replaced by [(Si,Al)O4] which fast atomic mobility and decease the viscosity of liquid phase, resulting the mullite nucleation and growth.

Keywords: Mullite, solid state reaction, tungsten trioxide

ABS 714

THERMODYNAMIC PROPERTIES OF GAS-CERAMIC COATINGS AND INGESTED CMAS CORRODENTS

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The thermodynamic properties of ceramic coatings and their reaction products with molten silicate debris are crucial to improve their durability in gas-turbine engines. An example involves the corrosion studies of thermal (TBC) and environmental (EBC) barrier coatings of gas turbines by molten silicate debris consisting of CaO-MgO-Al2O3-SiO2 system (CMAS). Here, we discuss some results measured by high temperature drop solution calorimetry, drop-and-catch calorimetry (DnC) and differential thermal analysis (DTA) techniques to obtain the thermodynamic properties of ceramic coatings for gas-turbine engines and their corrosion products. The enthalpies of solution of Y2Si2O7 and Yb2Si2O7 and 31YSZ, 16RESZ based coatings and apatite reaction products are moderately positive. However, 7YSZ shows somewhat different behavior. Apatite formation is only favorable over coating dissolution in terms of enthalpy for 7YSZ. The enthalpies of mixing between the coatings and the molten silicate are less exothermic for Yb2Si2O7 and CaYb4Si3O13 than for 7YSZ, indicating lower energetic stability of the latter against molten silicate corrosion. We also report for the first time the calorimetric measurements of the enthalpies of formation of rare-earth silicate based EBC coatings and apatites (rare-earth, RE = Y, Yb, Gd, Dy, Er, Nd and Sm). Implications of these results on predicting the stability field of the coatings, apatites and CMAS induced corrosion are discussed.

Keywords: Coatings, Calorimetry, Thermodynamics

ABS 708

A STUDY ABOUT NANOCOMPOSITE CERAMIC MATERIALS PROCESSED BY INJECTION MOULDING FOR A TEXTILE INDUSTRY APPLICATION

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The work presented here was developed under the framework of WhatCIM project that aims at developing new yarn guides for the textile industry. New nanocomposite ceramic materials and nanostructured coatings will be tested to overcome problems such as high wear and friction that have a negative impact on productivity. In order to obtain new technical ceramic components, given their complex geometric shape and functional specifications, the whole process of injection molding (CIM) at medium pressure (MPIM) will be developed.

The ceramics should have high wear resistance and very low friction coefficient to withstand the high speeds of textile polyester yarn while allowing for a smooth flow and preventing release and settling of oligomers at their surfaces. This is accomplished by obtaining fully dense materials or by coating them with hard, smooth and preferably conductive coatings by PVD. Therefore, the present work was aimed at investigating the relationship between the microstructure of alumina nanocomposites with the additives content and the sintering profile. The effect of manganese oxide, titanium oxide, magnesium oxide and silicium oxide, as sintering additives, was studied under different pressureless sintering curves. Sintering under non-oxidizing atmosphere with TiN particles was also attempted with the aim of reducing the electrical resistivity of the ceramic components. The microstructure and phase composition were evaluated by scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS) and X-ray diffractometry (XRD). Microstructural features were analysed and quantified and related with mechanical properties such as Vickers hardness, fracture toughness and Young´s modulus. Composites with the better characteristics will be used to produce a feedstock to be used in a CIM shaping process.

The CIM feedstock solids content was optimised based on the critical powder volume concentration determination, performed by torque rheometry. Different binders were tested and CIM process parameters were set based on their thermal characteristics assessed by differential scanning calorimetry (DSC) and thermogravimetry (TG). Molded test specimens were thermally debinded and sintered using the same profile used before. After the characterisation of PIM sintered materials, a comparison study was derived about the effect of press and injection moulded processes, and the effect of addition of nanoparticles into alumina material.

Keywords: Alumina, wear resistance, low electrical resistivity

ABS 707

THEORETICAL INVESTIGATIONS ON THE EFFECTS OF SOLUTE ATOMS ON HIGH TEMPERATURE MECHANICAL PROPERTIES OF ZrB_2

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Transition metal diborides (TMB2s) exhibit unique combination of excellent properties, which makes them promising candidates for extreme environmental applications. It is well-known that addition of compounds with Mo, W and etc. is beneficial to their high temperature mechanical properties. In this report, we will present our systematic theoretical investigations on effects of solute atoms (Nb, Ta, Mo and W) on high temperature mechanical properties of ZrB2 by first principles calculations. The positive effects of these solute elements may include: 1) solid solutions can reduce dislocation nucleation barrier, which assists the dissipation of deformation energy; 2) solute atoms can segregate to grain boundaries, enhance grain boundary strengths and pin grain boundary sliding at high temperatures; 3) solute atoms may further push the residual oxygen atoms away from grain boundaries.

Keywords: ZrB2,Solute Atoms, High-T Mechanical Properties

ABS 705

EFFECT OF SMALL AMOUNT OF ALUMINA ON SINTERING BEHAVIOR, STRUCTURE AND MECHANICAL PROPERTIES OF ZIRCONIA CERAMICS

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Objective The technical progress constantly presents new requirements for materials and devices. The lifetime and reliability of ceramic materials, which operate in aggressive environments and at high mechanical loadings, when the fracture of the device can be initiated by small damage on a surface, should be increased continuously. These trends leads to formation of a new method of material design creation – task oriented structure formation during sintering. The aim of this study is to show the effect of small amount of alumina addition on sintering behavior, structure and mechanical properties of zirconia ceramics.

Materials & Methods The ZrO2+3mol%Y2O3 (3Y-TZP) and ZrO2+3mol%Y2O3 +2wt%Al2O3, were synthesized by co-precipitation technique and traditional mechanical mixing. The powders and sintered specimens were characterized by XRD, TEM, SEM, EDS analysis. The sintering kinetics of all samples was investigated using a dilatometer DIL 402 PC. For the sintering mechanisms determination a constant rate of heating technique was used. The hardness and fracture toughness of the sintered samples were measured by the Vickers indentation technique. The fracture toughness values were calculated by Niihara equation for Palmqvist type cracks.

Results Addition of 2wt% Al2O3 in 3Y-TZP powder by co-precipitation technique leads to changing the mechanisms of nanoparticles sintering from volume diffusion (VD) to grain boundary diffusion (GBD). However, the consistent effect of milling process on 3Y-TZP+2wt%Al2O3 nanopowders, obtained by co-precipitation technique lead to reverse changing of diffusion mechanisms from GBD to VD with decreasing the activation energy level. During sintering of a mixed 3Y-TZP with 2wt%Al2O3 powders the VD mechanism is realized. According to the SEM data the different types of grain fracture and Al2O3 grains distribution in the zirconia matrix were found.
The fracture toughness value of the sintered 3Y-TZP was 5.9 MPa*m1/2. Addition of 2wt% Al2O3 in the 3Y-TZP by mechanical mixing method lead to increasing the fracture toughness value on 10%, but using the co-precipitation technique lead to increasing the K1C value up to 10,5 MPa*m1/2. The computer simulation of the crack propagation in different types of structures confirmed these results.

Conclusions It was shown that the evolution of structure of the zirconia – alumina composites and fracture toughness value depends on the method of powder preparation. Decomposition of unstable solid solution Al3+ in the ZrO2 lattice and Al3+ diffusion on a zirconia grain boundaries during sintering allow to create a set of composite structures by changing of the temperature regimes.

Keywords: zirconia, composite, structure

ABS 703

RELIABILITY OF CERAMIC COMPONENTS - THEORETICAL CONCEPT AND PRACTICAL EXPERIENCE

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More than 80 years ago Weibull published his pioneering paper on fracture statistics, which relates the probability of failure of brittle tensile specimens to the load amplitude und the volume under load. Later this concept has been extended to account for multiaxial and non-uniform stress fields and for time dependent damage caused by sub critical crack growth. This Weibull concept is the state of the art procedure for the mechanical design of ceramic components. It enables the pre-diction of the probability of failure in dependence of the applied load and the volume.
Unfortunately surprising and frequent failures of ceramic components some-times happen, which cannot be explained using this concept. In general they are caused by loadings, which are harmless for polymer or metallic components and have therefore not been considered in the analysis. But they may cause catastrophic failure of ceramics. Examples are deviations between planed and realized geometry, temperature differences in the component or contact damage. Improvements are possible by procedures which are - simply speaking - following good practice for designing and handling ceramic components.

Keywords: Probability of failure, Reliability, Good Practice

ABS 700

INVESTIGATION ON THERMAL SHOCK RESISTANCE OF ALUMINA-SPINEL REFRACTORY BRICK

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Objective Nowadays, spinel-containing refractories are widely used in the steel making industry. MgO-spinel and Al2O3-spinel bricks show improved slag penetration resistance in the steel ladle. Spinel phase in a refractory material possesses a good combination of physical and chemical properties such as high refractoriness, high mechanical strength and high resistance to chemical attack and much more resistance to hydration. Moreover, the spinel phase has a higher melting temperature (2135°C) than Al2O3 (2054°C) and it has a thermal expansion coefficient
(~8.4 ×(10)^(-6)/K) which is close to that of alumina (~8.8× 10^(-6)/K).
The main aim of this research is to determine thermal shock resistance which is one of the most important properties for refractory material. Thermal shock resistance is depended on many factors (for instance: modulus of elasticity, thermal expansion coefficient and etc.) which can determine refractory lining efficiency in the work atmosphere. In this work, we examine the thermal shock resistance of Al2O3-spinel refractory bricks and the parameters which are necessary to obtain.

Methods & Material The specimen used in this study were obtained from the Al2O3-spinel bricks and characterized in terms of bulk density, apparent porosity, cold crushing strength. Microstructural characterization was done by scanning electron microscopy (SEM), elemental analysis by EDX and the phase composition by X-ray diffraction (XRD). The thermal shock resistance applied according to C1525 ASTM standard.

Results The results demonstrate that the compositions were extensively micro-cracked after the quenching. The factors which controlling thermal stress resistance, as expressed by the R and R' parameters, of micro-cracked ceramics have been analyzed in some detail.

Conclusion The presented work covers the most significant current research trends of refractories for the steel industry, especially the influence of spinel phase on the thermal shock resistance of Al2O3 rich bricks. The effect of the spinel phase can be detected by increasing the quenching temperature on the thermal shock resistance.

Acknowledgment
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Keywords: thermal-shock properties, alumina-spinel brick, steel making industry

ABS 698

COMPRESSIVE CREEP OF SIC WHISKER AND SHORT SIC FIBRE/ TI3SIC2 MAX PHASE BASED COMPOSITES IN AIR

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Silicon carbide whisker (SiCw) reinforced Ti3SiC2 MAX phase ceramic matrix composites were fabricated by spark plasma sintering (SPS). The sintered composites were subjected to compressive creep in the temperature range and a stress range of 1000-1300 oC and 20-120 MPa respectively. 10 and 20 vol. % of SiCw were used to compare the creep behavior with monolithic Ti3SiC2. 20 vol. % SiCw/Ti3SiC2 had the highest creep resistance irrespective of the temperature and stress. At temperatures below 1100 oC the creep deformation behavior of 10 vol. % SiCw/Ti3SiC2 was similar to 20 vol. % SiCw/Ti3SiC2. At higher temperatures (1200-1300 oC) the measured strain values of Ti3SiC2 and 10 vol. % SiCw/Ti3SiC2 were similar. The high creep resistance of 20 vol. % SiCw/Ti3SiC2 can be attributed to a higher density of SiCw in the grain boundary of Ti3SiC2. The activation energy and the stress exponent were determined for all compositions.

Keywords: Compression,Creep,Ti3SiC2

ABS 687

INFLUENCE OF SILICON INFILTRATION ON THE MECHANICAL BEHAVIOR AND DAMAGE MECHANISMS OF CVI-PROCESSED SIC / SIC CERAMIC MATRIX COMPOSITE

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A long fiber reinforced ceramic matrix composite consists of three parts: the fibrous architecture, the interphase and the matrix. Each of these parts fulfills a specific role in the mechanical behavior of the material. More particularly, the matrix maintains the arrangement of the fiber bundle inside the preform without causing changes in their properties, protects them from the external environment and ensures the transfer of the load to the fibrous reinforcement. Several methods have been made possible to develop this matrix but so far the most commonly used remains the chemical infiltration process (CVI). This process, which is now well known, gives the possibility, particularly in the case of SiC, to process a high purity deposit. However, the porosity content after elaboration of the material is often too important. This high degree of porosity is a major disadvantage of this method of preparation since these pores, mainly of large size and with acute angles, can be considered as crack initiation defects within the CMC. In this study, liquid silicon was introduced into a SiC / SIC woven 2D monolayer to better understand the influence of porosities on the mechanical behavior of this model ceramic matrix composite. This silicon rises by capillarity and fills the residual porosity, modifying only slightly the constituent levels. A thorough characterization of the material produced before damage was initially carried out. Macroscopic tensile and shear tests were carried out in the axis of the fibrous reinforcement in order to characterize the mechanical behavior. On the other hand, from a microscopic point of view, push-out tests were conducted to better understand the influence of silicon on interfacial bonds. After mechanical tests, the tested parts were again characterized, in particular by scanning and transmission microscopy, to know the mechanisms of material failure. It turns out that the two materials, either Si infiltrated or only CVI-processed, have a different mechanical behavior. However, more than an influence of the residual porosity, this difference could be attributed to the more or less marked presence of residual stresses in the material.

Keywords: silicon infiltration,mechanical behavior,CVI-processed SiC / SIC CMC

ABS 675

SYNTHESIS AND PROPERTIES OF (Zr,Ta)B_2 CERAMICS

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Zirconium diboride containing solid solution additions of tantalum ranging from 0 to 6 at% were synthesized by reactive hot pressing of zirconium and tantalum hydrides and amorphous boron. Microstructural analysis demonstrated that the (Zr,Ta)B2 ceramics reached nearly full relative density and were nominally phase pure. Analysis of x-ray diffraction data revealed that tantalum was fully incorporated into the ZrB2 structure and that the lattice parameters decreased with increasing tantalum addition. The mechanical properties that were measured included Vickers' hardness, flexure strength, and fracture toughness. Elastic properties were measured by impulse excitation and resonant ultrasound spectroscopy. The thermal properties measured included thermal diffusivity, heat capacity, and coefficient of thermal expansion. Properties were tested from room temperature up to 2000° C. Changes in properties were analyzed to determine the effects of tantalum content on ZrB2 and to guide future studies into the effects of additives and impurities on the processing and properties of diboride-based ultra-high temperature ceramics.

Keywords: Zirconium Diboride, Mechanical Properties, Elastic Properties

ABS 668

MULTISCALE OBSERVATION OF THE SELF-HEALING PHENOMENA IN A CERAMIC MATRIX COMPOSITE

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Ceramic-Matrix Composites (CMC) are made of ceramic fibers embedded in a brittle ceramic matrix subject to multi-cracking, yielding a “damageable-elastic” mechanical behavior. The crack network resulting from local damage opens a path to oxidative/corrosive gas diffusion towards fibers. The associated degradation by corrosion leads ultimately to failure of the composite under static fatigue in high-temperature oxidative conditions. In Self-healing CMC (SH-CMC), oxidation of the crack walls leads to the formation of a sealing oxide that forms a plug and limits the gas diffusion towards the fiber. This mechanism, called “healing”, delays considerably the fiber degradation and enables longer lifetime. Thus, SH-CMCs can reach extremely long lifetimes even under severe thermal, mechanical and chemical solicitations. However, crack-healing is a complex phenomenon which is difficult to characterize. Therefore, the ambition of this work is to provide reliable experimental data about the healing mechanism.

The crack healing capability of SH-CMCs with a pyrocarbon (PyC) interphase was studied by means of thermogravimetric analysis (TGA) coupled with a mass spectrometer (MS) and X-Ray micro-computed tomography (µCT) performed on flat model cracks in a real material. TGA were performed in the 450-800°C temperature range in dry and wet air (up to 10 vol.% H2O). MS was used to monitor carbon oxides formation during TGA in the different experimental conditions. µCT were performed before and after ageing in the TGA device. Observations of the composite cross-section are finally performed by means of SEM, EDS and Raman spectroscopy.

SH-CMCs crack healing capability relies on the formation of a borosilicate glass sealant. Its composition, formation kinetics and volatilization kinetics depend on both temperature and the moisture content in the gaseous environment. Therefore, these parameters have a major influence on the healing time of the crack, the recession rate of B4C layers and the PyC consumption rate. As crack healing limits the PyC oxidation, a drop of the signal related to carbon oxides obtained with MS is thus a good healing indicator. B4C recession rate are determined from comparison of the 3D scans obtained before and after ageing. PyC consumption rate along the crack are determined from Raman spectrometry mapping performed on cross-section. These quantitative data demonstrate that healing time increases with water vapor content and decreases with temperature. Consequently, B4C recession and PyC consumption are slower when healing time is decreased.

Keywords: Self-healing CMC,TGA,µCT

ABS 324

THE EFFECT OF MECHANICAL ACTIVATION ON SYNTHESIS AND PROPERTIES OF MgAl2O4 CERAMICS

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Magnesium aluminate, MgAl2O4, and other alumina-based spinels are refractory ceramics with high hardness and resistance to chemical attack while also being possible microwave dielectrics. Pure MgAl2O4 can be optically transparent when fully dense. Spinels exhibit inversion, which results in disorder among occupancy of A and B site cations. The goal of this study was to examine the effects of mechanical activation and composition on the temperature required for spinel formation and the site occupancy in the resulting spinel.

MgAl2O4 was produced by solid state reaction between MgO and alpha-Al2O3. The starting powders were mixed by ball milling to homogenize the powders without significant particle size reduction. Mechanical activation of mixed powders was performed in a high-energy planetary ball mill in air for 1 h. Powders were compacted at 300 MPa. Heat treatments were performed in air, at temperatures ranging from 1200 to 1500 °C with 2 h dwell time, to determine the amount of spinel formation as a function of temperature. Phase composition and microstructure of initial powders and heated samples were determined by means of X-ray diffraction, particle size analysis, and scanning electron microscopy. The influence of milling and consolidation parameters were studied by electrical measurements and mechanical characterization.

The main results of this study were that mechanical activation for 60 minutes initiated a mechano-chemical reaction, and resulted in spinel formation at much lower temperatures than within non-activated powders. Microstructures of ceramics sintered below 1400 oC indicated that final stage sintering started at much lower temperatures for activated samples than for non-activated samples.

Changes in microstructure parameters, as a consequence of mechanical treatment and subsequent heating of investigated powder mixtures, strongly affect electrical and mechanical properties of the final ceramics.

Keywords: mechanical activation, sintering, spinel

ABS 655

ELECTRICALLY CONDUCTIVE AND MECHANICALLY STRONG GRAPHENE/MULLITE CERAMIC COMPOSITES FOR HIGH-PERFORMANCE ELECTROMAGNETIC INTERFERENCE SHIELDING

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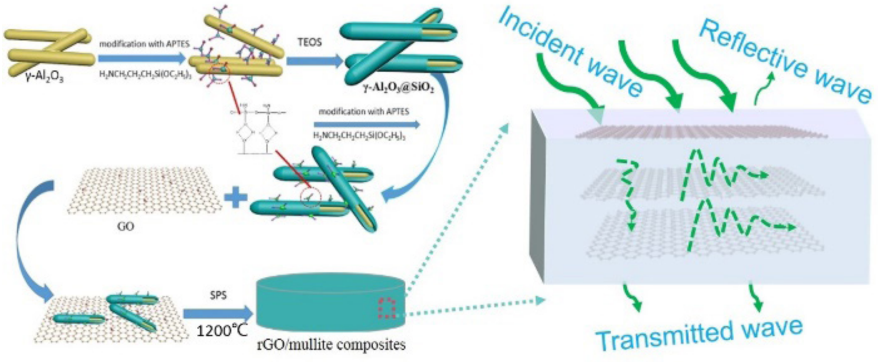
Ceramic composites with good electrical conductivity and high strength that can provide electromagnetic interference (EMI) shielding are highly desirable for the applications in harsh environment.It is well known that mullite shows high strength and thermal shock resistance at elevated temperature and also possesses the merit of low density that is very suitable to be exploited as the matrix of EMI shielding composite for reducing the weight. However, the high sintering temperature of mullite powder prevents the incorporation of highly efficient carbon based microwave absorbent such as graphene.

In this study, lightweight, highly conductive, and strong mullite composites incorporated with reduced graphene oxide (rGO) are successfully fabricated by spark plasma sintering at merely 1200 degree C using the core-shell structured γ -Al2O3@SiO2 powder as a precursor.

The transient viscous sintering induced by the γ -Al2O3@SiO2 precursor not only prohibits the reaction between mullite and rGO by greatly reducing the sintering temperature, but also induces a highly anisotropic structure in the rGO/mullite composite, leading to an extremely high in-plane electrical conductivity and magnitude lower cross-plane electrical conductivity in the composites.

As a result, very large loss tangent and EMI shielding effectiveness (>32 dB) can be achieved in the whole K band with extremely low rGO loading (less than 1 vol %), which is beneficial to maintain a good mechanical performance in ceramic matrix composites. Accordingly, the rGO/mullite composites show greatly improved strength and toughness when the rGO content is not high, which enables them to be applied as highly efficient EMI shielding materials while providing excellent mechanical performance.

Keywords: ceramic matrix composite, mullite, graphene



ABS 638

ENHANCED WEAR RESISTANCE OF ENGINEERED GLASS-CERAMIC BY NANOSTRUCTURED SELF-LUBRICATION

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In this work, a new glass-ceramic family with high crystallinity, >90 %, and a unique micro-nanostructure has been successfully designed following a fast sintering processing route. These engineered glass-ceramics are based on albite and anorthite crystallizations, feldspars which are very used in ceramic materials. These engineered glass-ceramics result in a simultaneous improvement of flexural strength, microhardness, fracture toughness and tribological properties regarding standard materials used in tile industry.

Flexural strength values up to 111 MPa and microhardness values of 9.5 GPa are measured, supposing an improvement of ~ 60 % regarding current glazes for ceramic floor tiles for high transit areas and ~ 7 % regarding the best-reported value in literature for a glass-ceramic material. The hierarchical micro-nanostructuration of these glass-ceramics favours crack deflection, which implies a reduction of brittleness in these materials and a consequent increase of fracture toughness of ~ 40 % regarding a standard glass-ceramic. Tribological properties are also evaluated, showing a decrease in the friction coefficient (μ) of ~ 36 % and a surprising reduction of the wear rate (WR) larger than one magnitude order, in both micro-nanostructured glass-ceramics, concerning a standard glaze tested. Worn tracks analysed by Multi-Mode Optical Profilometry and FE-SEM measurements revealed that nanocrystals present in the microstructure work as solid lubricants, favouring sliding over their surface and noticeably reducing μ, WR and the surface damage suffered. Wear mechanism undergone by both glass-ceramics is unlike other glass-ceramics, similar to a polishing process, without any apparent material spalling.

All of these findings make hierarchical micro-nanostructured glass-ceramics very promising candidates to be used in high performance self-lubricating applications, being suitable for high pedestrian traffic applications and also supporting machinery traffic, which will enable a considerable improvement of mechanical behaviour and durability of tiles.

Keywords: micro-nanostructure, glass-ceramic, solid lubricant

ABS 633

AN ECONOMIC AND FACILE METHOD FOR GRAPHENE OXIDE PREPARATION FROM GRAPHITE POWDER

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Objective The aim of this work is to develop a new method for preparing multi-layered graphene oxide powder using commercially available micro-sized graphite powder as raw material. The graphite powder was milled by high speed attritor mill to reduce the particle size of graphite to nanometre and to exfoliate the graphite into multi-layered graphene particles. The graphene particles were then oxidized into graphene oxide using the combination of strong oxidizing agents and thermal oxidizing and sonication.

Materials & Methods The raw material was synthetic graphite powder. The graphite was milled in high efficient attritor mill with rotation speed of 3000 rpm for 10 hours in ethanol media. The prepared multilayer graphene (MLG) nanosheets were then treated in three steps. First, the powders were dispersed in cc. HNO3 solution and stirred at 80 C for 4 hours then 50% H2O2 was added to the dispersion under continuous stirring and kept at room temperature for 16 hours. Second, the powders were put into oven and heat treated at 850 C for thermal oxidation. Finally, the treated powders were dispersed in ethanol and sonicated in ultrasonic bath for 3 hours at 70 C to examine the effect of ultrasound on the exfoliation rate of graphene oxide multilayers.

Results According to SEM characterization, typical wrinkled lamellar and multilayered structure of particles were visible in the case of MLG powder. The thin platelets were closely stacked and compacted. After chemical oxidization treatment the graphene become even more exfoliated and individual graphene oxide sheets were observed with wrinkled edges. After thermal oxidization, the morphology of GO particles changed, smaller sized platelets (100-600 nm) have appeared along with the larger plates. The edges of platelets have become more corrugated upon oxidization. Ultrasonication for a long time visibly reduced the size of the graphene oxide particles and small, flake-like particles also appeared. The size of the graphene oxide particles varied within large scale, between 50 nm and 500 nm.

Conclusions Graphene oxide powder were successfully prepared from commercially available graphite powder by applying appropriate exfoliation, chemical and thermal oxidization processes.
The morphological and structural characterization of powders revealed the changed morphology of graphene oxide particles compared to MLG, which might prove that the oxidization processes were successful.

Keywords: graphene oxide, MLG, attritor mill

ABS 607

VIOLATION OF THE CLASSICAL LAW FOR GRAIN GROWTH IN TWINNED BORON CARBIDE POLYCRYSTALS UNDER ELECTRIC FIELDS

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This work demonstrates that grain-growth kinetics is drastically dependent on the presence of twin steps at the grain boundaries in B4C ceramics sintered by spark plasma sintering. The conjunction of high temperature gradients with large compressive stress when a pulse electric current passes through the ceramic powders gives rise to an intense twinning–detwinning formation. These forming steps at the grain boundaries change the grain mobility drastically. Therefore, a new ‘exotic’ law for grain-growth kinetics is found and validated at different temperatures and dwell times. The time dependence of the grain size is proved to follow one law which has the same functional form as the Bose-Einstein distribution law.

Keywords: Grain growth, spark plasma sintering, twinning

ABS 605

PROPERTIES OF TZPs MADE FROM RARE EARTH OXIDE CO-STABILIZED POWDERS MADE BY COATING AND MECHANICAL ALLOYING PROCESS

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Zirconia ceramics are well known for good mechanical properties such as high strength and high toughness. State-of-the-art 3Y-TZP is manufactured from coprecipitated powder and achieves high strength but only moderate toughness. Stabilizer coating of monoclinic powder by wet chemical routes or by intensive mechanical alloying of monoclinic powder and rare earth oxide stabilizer are alternative powder preparation routes. Such powders retain a stabilizer gradient and combine high toughness with improved ageing resistance. However, they are commercially not available.

Three different stabilizer systems, 3Y-TZP, 1.5Y1.5Nd-TZP and 1.5Yb1.5Sm-TZP were tested in order to evaluate the quality of powders derived from the wet chemical process and the mechanical alloying route. Stabilizers were either introduced by coating monoclinic zirconia with rare earth nitrates which were subsequently thermally decomposed to oxides or added by a high energy milling process of zirconia and stabilizer oxides dispersed in 2-propanol at different milling intensities.

TZP samples derived from these starting powders were hot pressed at 60 MPa pressure at different sintering conditions between 1250°C and 1350°C for 1 or 2h and then tested with respect to mechanical properties, phase composition, microstructure and ageing resistance. The study shows promising results. By mechanical alloying larger batches of powder can be produced at significantly reduced effort and cost. However, the stabilizer formulation i.e. the ionic radius of rare earth cations, the thermodynamic equilibria and the diffusion kinetics seem to have a strong influence on the efficiency. In case of 1.5Y1.5Nd-TZP materials from both routes show almost identical mechanical properties, a bending strength of >1000 MPa and a toughness of 13 MPa m^1/2 are possible. In case of 1.5Yb1.5Sm-TZP and 3Y-TZP the coated powders lead to slightly enhanced strength and toughness.

Keywords: co-stabilized zirconia, mechanical properties, powder preparation

ABS 597

INFLUENCE OF THE MEASUREMENT METHOD AND SAMPLE DIMENSIONS ON THE YOUNG’S MODULUS OF OPEN CELL FOAM ALUMINA

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Within this study the influence of the sample shape, the cell size and the measurement method on the Young’s modulus E of open cell foam alumina was investigated. The measurement methods used for the determination
of E were the impulse excitation technique, the longitudinal ultrasonic mea- surement, the quasi-longitudinal ultrasonic measurement and the three point bending technique (3PB). Three different sample dimensions (rectangular bar differing in the cross section but not in length) and cell sizes (10, 20 and 30 pores per inch according to the manufacturer) were investigated.
The samples (bars) comprising the smallest height, yielded the highest E values for all measurement methods due to its processing, causing higher densities and homogeneity and hence leading to increased E values. Further- more, its smaller area moment of inertia results in a higher beam deflection for a fixed force applied in 3PB. Thus, in the case of this shape, the forces involved during the 3PB tests were much lower and a smoother test could be performed and resulted in higher E values. Measurement difficulties were found for the determination of E by the impulse excitation technique at large cell sizes (10 and 20 ppi). The obtained E values differed significantly from those obtained by ultrasonic and 3PB tests. This was attributed to a reduction of the vibrating surface beneath the microphone capturing the audio signal. Ultrasonic methods performed robustly, however have to be conducted with care (e.g. Poisson’s ratio assumption).
Hence, the use of ultrasonic measurement methods can be recommended for open cell foam structures investigated in this study, whereas the IET has its limitation especially for samples containing large macro pores.

Keywords: Elastic properties, reticulated foam, method comparison

ABS 588

MAX PHASES AND DERIVATIVE BINARY CARBIDES FOR ISOL TARGETRY

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The Isotope Separation On-Line (ISOL) technique consists of on-line evaporation, selective ionization, acceleration, and mass purification of radioisotopes produced in a target material irradiated by an accelerated particle beam. ISOL target material requirements include refractoriness, in order to withstand the high-power beam deposition, and optimized porosity, so as to enable the fast evaporation of short-lived reaction products. Microporous binary carbide ceramics produced by the thermal decomposition of MAX phase ternary carbides, such as Ta4AlC3, Ti3AlC2 and Ti2AlC, may constitute an innovative and promising path towards development of materials for ISOL targets. Ta and Ti-based target materials were proposed for the production of specific isotopes utilized in nuclear medicine research. The Mn+1AXn phases containing A elements with relatively high vapor pressures, such as aluminum (Al), are known to be unstable at high temperatures in vacuum, decomposing into porous binary Mn+1Xn phases and A-element vapors. The thermal decomposition in vacuum of Ta4AlC3, Ti3AlC2 and Ti2AlC into Al vapor and TaCx and TiCx respectively, was investigated in the 1200-1800°C range as a possible route towards ISOL target material development. An advantage over the relatively simpler use of fine commercial carbide powders lies in the machinability of the MAX phases before compaction, shaping and dealumination heat treatment. The decomposed Ta–C and Ti–C materials were characterized in terms of phase assembly and microstructure/porosity. Moreover, the formation of new MAX phases in the Ta–Hf–Al– C and Ta–Nb–Al–C systems was investigated, as a first step towards the production of porous complex carbides with the (Tax,Hf1-x)Cy and (Tax,Nb1-x)Cy general stoichiometries based on the same thermal decomposition approach.

Keywords: MAX phases, Carbides, ISOL

ABS 566

SILICON CARBIDE-GRAPHENE COMPOSITES WITH HIGH ELECTRICAL AND THERMAL CONDUCTIVITY

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Objective The aim of the present contribution was to investigate the influence of graphene nanoplatelets (GNPs) and graphene oxide (GO) additions, orientations of the graphene layers and effect of annealing on functional properties of SiC-graphene composites.

Materials & Methods Composite powders with different amount of GNPs from 1 to 10 wt. % or 1 wt. % of GO were prepared. The appropriate amounts of GNPs/GO were dispersed in distilled water by intense ultrasonication. Afterwards, SiC powder with 1 vol.% Y2O3–Sc2O3 additives were added into the suspensions and homogenized on magnetic stirrer. The prepared suspensions were sprayed into a liquid nitrogen and subsequently lyophilised. Such prepared powders were sintered in rapid hot press (RHP) at 2000°C for 30 min with a pressure of 50 MPa under nitrogen atmosphere.

Results Electrical conductivity and thermal diffusivity were investigated as a function of amount of graphene, its orientation in SiC matrix and effect of annealing. With increasing amount of graphene the electrical conductivity increases in both measured directions.
The thermal diffusivity decreased with increasing GNPs content in direction perpendicular to graphene layers, e.g. from 63.7 mm2/s for 1 wt. GNPs % to 33.4 mm2/s for sample with 10 wt. % of GNPs. The resulting decrease of thermal diffusivity of SiC-graphene samples indicates that the phonons scatter on pores, defects and boundaries between the GNPs and SiC matrix. Moreover, the intrinsic thermal properties of GNPs are anisotropic (lower in c-direction compared to a-direction) and could influence the thermal diffusivity of composites.
The thermal diffusivities measured in direction parallel to GNPs increased significantly up to 104.4 mm2/s for sample with 5 wt. % of graphene after annealing. This indicates that graphene layers in parallel direction could be effective in formation of conductive phonon channels. Moreover, by annealing of samples the grain size increased and the lattice oxygen decreased. Beneficial influence of post sintering annealing in all cases was confirmed.

Conclusions Almost fully dense SiC-Y2O3-Sc2O3 composites with addition of either GNPs or GO were prepared by RHP. The thermal diffusivity of sample with 5 wt.% of GNPs in parallel direction to GNPs remarkably increased after annealing to 104.4 mm2/s from value 72.3 mm2/s measured for the reference sample (without addition of graphene and annealing). At the same time the electrical conductivity increased from 1400 S/m (for reference sample) to 9402 S/m for composite with 5 wt. % of GNPs.

Keywords: SiC-graphene, thermal diffusivity, electrical conductivity

ABS 543

THETA-ALPHA COMPOSITE POWDERS FOR LOWER TEMPERATURE VACUUM SINTERING OF HIGH TRANSLUCENT ALUMINA

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The character of θ-+α-Al2O3 powder systems for lower temperature sintered high translucent alumina at vacuum is investigated. The composite powders that consist of the two sizes α-Al2O3 particles and a small amount of θ-Al2O3 were prepared. The particle sizes of α-Al2O3 are 200 nm and 50-100 nm, and the particle sizes of θ-Al2O3 are 20 nm. The 50-100 nm α-Al2O3 powder is smaller than the commercial powder. Due to the finer α-Al2O3 powders and the Furnas model that induced higher packing density of the compact, the composite powder can be easily sintered at temperature as low as 1600 oC. And the translucent alumina with high light transmittance can be obtained, while the mean grain size remains <2 µm.

Keywords: Alumina, packing density, vacuum sintering

ABS 539

INCONEL 625 - WC COMPOSITE SYSTEMS

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This research presents Laser Cladding of metal matrix composite: Inconel 625 - tungsten carbide system. The protective layer of composite coating was deposited on pure Inconel 625 substrate using high power fiber laser. Initial mixtures containing different amount of tungsten carbide were mixed with additional binder to achieve homogenous distribution of carbide in whole volume of mixture. Samples obtained by laser processing are characterized by increased hardness and good connection to substrate. The microstructure analysis performed by means of SEM - EDS and TEM - EDS showed that both primary (WC) and secondary carbides were present in material after processing. This indicates partial dissolution of small WC particles during the process. Appearance of fishbone-like nanostructures shows that topologically close-packed (TCP) phases formed due to rapid cooling of the material. The SEM-EDS mapping revealed segregation of Mo and Nb to interdendritic region and formation of secondary carbides of these elements. Improvement of hardness was observed in composite. It is about 25% higher than hardness of pure Inconel 625 sample prepared in the same conditions with use of same process parameters. DTA analysis of composite samples shows decrease of melting temperature of composite systems in comparison to pure Inconel 625. The evolution of microstructure in different heating conditions was investigated.

Keywords: laser processing, metal matrix composites, electron microscopy

ABS 534

PROCESSING OF HOLLOW STRUCTURES FROM SEMI-FINISHED TEXTILE PRODUCTS IN CERAMIC COMPONENTS

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Thanks to the development in Additive Manufacturing (AM) in recent years, ceramic components with defined hollow structures and a minimal geometrical size and resolution, are reaching new dimensions in their realization. However, the production time, depending on the size of the component, is time-consuming and costly.

In the context of a publicly funded project, an alternative cost-effective and time-saving process, which avoids AM, was developed using a combination of textile and ceramic shaping technology to manufacture 2D and 3D ceramic structures with defined internal channels. For achieving those hollow structures, textile elements were integrated into ceramic materials shaping processes such as tape casting or slip casting. Selected textile raw materials like embroideries and knitted fabrics where used as semi-finished products and served as lost-mold components during the part production. After debinding and sintering, they create the final channel structures inside of the ceramic part.

For this purpose, the established shaping processes of slip casting and tape casting were both modified by applying a multi-step processing. In both cases, the textile material was applied firstly onto the initial thin tape layer (in undried state) and respectively, onto the core part in the slip cast mold (in dried state). In the next step, the textiles were covered by either a second or the final tape layer/slip cast material. In the subsequent heat treatment, comprising debinding and sintering, the binders of the ceramic component and the yarn burn out without residue. The desired hollow structures remain in the ceramic component. As a first demonstration, a ceramic sleeve with a meandering internal channel was achieved by applying the multi-step slip casting approach. In a second demonstration a ceramic flat substrate with an integrated channel structure was achieved by applying the multi-step tape casting. In addition, it was shown that resulting channel systems can be functionalized by coating the inner surface with a metal or zeolite layer.

Thus, the usage of such complex components becomes particularly interesting for high temperature or lightweight applications as well as for processes requiring high chemical resistance, certain mixing ratios and/or chemical/biological/catalytic activity (e.g. micro reactors, heat exchangers etc.).

Keywords: multi-step processing, textile element, internal channel

ABS 532

NEW ZEOLITE-ALUMINA COMPOSITE MATERIALS - DEVELOPMENT AND INVESTIGATION

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In this work, Zeolite-Alumina ceramic composite materials were developed by the on the basis of natural zeolite from Tokaj region (Hungary) and MOTIM Al2O3 powder using mechanical activation and reactive sintering methods.

The structure, morphology, thermal and mechanical characteristics of the complex composite structured were investigated using different characterization techniques including, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermo-analytical analyzer (DTA) and universal materials testing machines, The XRD investigation of the natural zeolite from Tokaj region has shown many phases with different contents of minerals like montmorillonite, quartz, cristobalite, clinoptilolite, and calcite. Meanwhile after mechanical activation, compaction and sintering of the Zeolite-Alumina new compositions of ceramic composite were achieved with increased mechanical and physical properties. In this presentation they would like to introduce these new ceramic composite materials and their properties like micro-structure, mechanical strength, hardness, etc.

Keywords: Zeolite, Composite materials, reactive sintering

ABS 519

THERMOMECHANICAL CHARACTERIZATION OF AN ALUMINA SPINEL REFRACTORY FOR STEEL LADLE APPLICATIONS

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Objective The presented research has been performed in the framework of ATHOR - a European project involving 15 Early Stage Researchers, cooperating within international network of 7 academic and 8 industrial partners. One goal of the project is to develop a complete numerical model of steel ladle. In this context, the present study aims to provide input data for modeling and improve understanding of relationships between material's microstructure and thermomechanical properties. These investigations are focused on alumina spinel refractory bricks that, due to their high performance, achieved especial interest from industrial point of view.

Material & methods The microstructure of the alumina spinel refractory bricks consists of a fine alumina spinel matrix and coarse alumina inclusions. This material has been fired during several hours at 1700°C and the initial spinel content is about 20 wt%. In order to evaluate thermomechanical properties in operating conditions (up to 1550°C for a steel ladle), experimental characterization has been performed using specialized high temperature equipment, such as ultrasonic measurements, uniaxial tensile test, acoustic emission measurements, as well as more classical techniques, including dilatometry, XRD and SEM. In fact, Young's modulus, CTE and stress-strain law in tension (compression) are the first key thermomechanical parameters that are required for FEM modelling. Additional investigations by wedge splitting coupled with refined DIC have also been performed to quantify fracture energy and observe crack propagation. Obtained results have been interpreted with the help of structure and microstructure evolutions of the material.

Results The curve of Young's modulus evolution during thermal cycle shows a hysteresis loop, which is mainly related with pre-existance of microcracks. Sample elongation during dwell at high temperature, might be caused by the interactions between alumina and spinel grains. Moreover, non-linear mechanical behaviour, being typical for materials containing network of microcracks, was detected both on the stress-strain and on the load-displacement curves obtained by tensile and wedge splitting tests, respectively.

Conclusions Pre-existing microcracks and relatively big alumina inclusions induce energy dissipation phenomena, that contribute to slight increase of crack propagation resistance, strain-to-rupture and thermal shock resistance. Moreover, the material's expansion during dwell could be advantageous for promotion of joints closure mechanism between bricks at the hot face of the lining, thus limiting corrosion.

Acknowledgements
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Keywords: alumina-spinel refractory, microstructure, mechanical properties

ABS 501

HYDROTHERMAL CORROSION BEHAVIOUR OF ENVIRONMENTAL BARRIER COATINGS FOR SILICON CARBIDE FUEL CLADDING APPLICATIONS OF LIGHT WATER REACTORS

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After the Fukushima accident, various accident-tolerant fuel (ATF) cladding concepts such as coated Zr alloys, FeCrAl alloys, Mo-based alloys, SiC-based composites has been proposed. Among them, the silicon carbide (SiC)-based composite has shown the exceptional performance under the accident conditions of light water reactors (LWRs) such as excellent corrosion resistance in hot steam and high temperature strength above 1200oC. However, SiC-based composite tends to dissolve into the coolant water in LWR primary coolant environments. Also, the formation of microcracks may cause the problem such as the fission products within the fuel cladding leaking into the coolant water. In order to prevent the permeation of gaseous fission products and to prevent the dissolution of the SiC-based fuel cladding by hydrothermal corrosion, we applied Ti-based and Cr-based environmental barrier coatings (EBCs). We evaluated the hydrothermal corrosion behavior of various EBCs in the pressurized water environment.

Keywords: Accident Tolerant Fuel Claddin, Environmental Barrier Coating, Hydrothermal Corrosion

ABS 496

JUDICIOUS SELECTION OF SINTERING ADDITIVES FOR ACHIEVING HIGH-PERFORMANCE SILICON CARBIDE CERAMICS

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Tailoring microstructure and additive composition are critical components for achieving high-performance silicon carbide ceramics. Significant improvements in the electrical, thermal, and mechanical properties of liquid-phase sintered silicon carbide (LPS-SiC) ceramics have been obtained by tailoring the chemistry of sintering additives in the last decade. The role of additives in the sintering of SiC ceramics can be regarded as not only densification aids, but also key elements for achieving high-performance properties, since electrical, thermal, and mechanical properties of SiC ceramics are influenced by the composition of additives as well as the microstructure of the resulting ceramics.

In this paper, four examples of the tailoring additive composition for achieving high performance SiC ceramics will be presented: (1) Y2O3–Gd2O3 additives for electrically conductive SiC ceramics (>110 ohm-^{1}-cm-^{1}) , (2) Y2O3–Sc2O3 additives for thermally conductive SiC ceramics (>260 Wm-^{1}K-^{1}), (3) Y2O3–Sc2O3–MgO additives for high-strength SiC ceramics (>1 GPa), and (4) a Y2O3 additive for heat-resistant SiC ceramics (550 MPa at 1700oC).

Considering the decisive influence of the additive composition on the development of microstructure, grain boundary structure, and the resulting electrical, thermal, and mechanical properties of LPS-SiC ceramics, the compositions of sintering additives must be carefully selected to achieve the desired properties. From my point of view, future work in this field should be directed toward the investigation of suitable compositions and microstructures for specific target applications, focusing on the deliberate tuning of factors affecting the properties of the final LPS-SiC ceramics.

Keywords: silicon carbide, additive composition, microstructure

ABS 491

ZIRCONIA - BASED CERAMICS REINFORCED WITH SUPERHARD CUBIC BORON NITRIDE PARTICLES OBTAINED BY SPARK PLASMA SINTERING

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The aim of presented studies was to obtain a new generation of zirconia-based matrix composites reinforced with superhard cubic boron nitride particles (cBN), having improved mechanical properties, especially higher fracture toughness and wear resistance in reference to ordinary zirconia/alumina ceramics.
Fine zirconia powder (40 nm) and zirconia/alumina composite powder (ZrO₂/20 wt. % of Al₂O₃, 70 nm) were used for the matrices. Reinforcing phase was cubic boron nitride (3–6 μm) in an amount of 20 to 50 vol. %. Spark Plasma Sintering (SPS) method was chosen for composites preparation in order to study the behaviour of metastable cubic boron nitride during sintering of ZrO₂ + cBN and ZrO₂/Al₂O₃ + cBN composites at low pressure (about two orders of magnitude lower than pressure of thermodynamic stability of cBN). Relatively low sintering temperatures were used to avoid the undesired reverse transformation of cBN to hexagonal graphite-like form. The microstructure and phase composition as well as physical and mechanical properties of the resulting composites were investigated. In the ball-on-disc tests, the coefficient of friction and the specific wear rate of the sintered samples were determined.
A full densification of matrix materials sintered separately was achieved at 1300 °C and 1400 °C for ZrO₂ and ZrO₂/20 wt. % Al₂O₃ respectively. The addition of cBN to ZrO₂ matrix didn't affect sintering temperature of material but in the case of ZrO₂/20 wt. % Al₂O₃ matrix cBN caused decrease of sintering temperature even by 250 °C. Densification curves of composites with cBN have maxima around the temperatures of 1150 – 1300 °C depending on composition. Those maxima are caused by two opposite processes: densification of material during sintering and cubic to hexagonal boron nitride phase transition at higher temperatures.The addition of cBN to ceramic matrices resulted in increase of Young's modulus (up to ~300 GPa) and fracture toughness (up to ~7 MPa*m^{1/2}). The composites have four times better wear resistance than ceramic matrices sintered without cBN.

It is possible to obtain ceramic composites containing cBN at not equilibrium conditions provided by SPS method. Optimisation of matrix composition as well as sintering temperature is essential to avoid undesired reverse transformation of cBN to soft hexagonal phase. The addition of cBN to ZrO₂ and ZrO₂/Al₂O₃ matrices improved their mechanical properties and wear resistance. SPS can thus be regarded as a promising alternative to expensive High Pressure – High Temperature (HPHT) methods in the manufacturing of composites with metastable cBN phase.

Keywords: zirconia, cubic boron nitride, Spark Plasma Sintering

ABS 486

TUNGSTEN CARBIDE – NICKEL CERMET AS AN ALTERNATIVE PLASMA-FACING MATERIAL FOR FUSION APPLICATION

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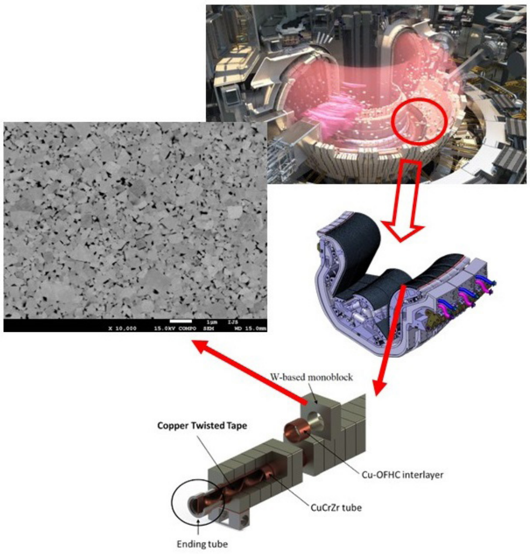
Tungsten-based composites are still considered as primary candidates for plasma facing materials in fusion reactors. They have good properties, but one disadvantage of matrix material W is its thermal instability. At moderate temperatures (<400 °C) it's brittle and at high temperatures (>1200°C) the material recrystallizes and loses good mechanical properties. That is why we propose substitution of matrix material with thermally more stable; tungsten carbide. Ductility of this brittle ceramic material can be improved with the addition of metallic binder phase. So far cobalt is the best choice, but for fusion application, Co has to be replaced with low activation elements. Possible substitutions are nickel or iron, but because of high affinity to oxidation of iron, this candidate is less appealing option. The proposal is to use nickel as a binder phase in WC cermet. Tungsten carbide and nickel powder are homogenised in a planetary ball mill. The mixed suspension is then freeze-dried and dry powders are sintered using Field Assisted Sintering Technique (FAST) at different sintering regimes. As-sintered WC-Ni composites' (cermets) mechanical properties (flexural strength and Vickers hardness) and density were measured. Samples' microstructure was examined using SEM, while phase composition was determined by XRD.

However, all samples' densities were above 96 % TD. Sample with the best mechanical properties was WC – 10 wt. % Ni, prepared with FAST at 1350 °C for 5 min with applied pressure of 60 MPa. Flexural strength and hardness of the sample were 1850 MPa and HV/10 17.7. Mechanical properties of the composite with a concentration of 20 wt.% Ni decreases, due to the excess of the binder phase. A lower concentration of binder phase reveals pores in the microstructure, which also decreases flexural strength to 1480 MPa. If applied pressure is too high (100 MPa), the liquid binder phase is pushed out of the sample during sintering, consequently, the flexural strength decreases to 1670 MPa. XRD analysis shows mainly hexagonal WC and fcc Ni as well as the minor quantity of intermetallic phase Ni_6C, due to the deficiency of carbon during sintering.

In the future work, we will eliminate carbon deficiency and formation of brittle Me_6C phase with the addition of carbon precursor in the powder mixture. Further analysis of mechanical properties on elevated temperatures (<1000 °C), as well as aged samples on high temperature, will be made since the material will be subjected to high temperatures in the fusion reactor.

Keywords: Tungsten carbide, Cemented carbides, Fusion



ABS 466

PARTICULATE INDUCED SELF-HEALING MATERIALS FOR ENVIRONMENTAL BARRIER COATINGS

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Several types of environmental barrier coatings (EBCs) have been developed to protect non-oxide monolithic ceramics and ceramic matrix composites (CMCs) against corrosive attack. Especially rare-earth silicates exhibit beneficial properties regarding corrosion protection and thermal expansion behaviour. However, the occurrence of cracks leads to local loss of protection and limits the long-time protection.

The addition of non-oxide particles in rare-earth silicates to achieve self-healing behaviour was examined. The investigations also comprised long term burner rig tests and resulted in a deeper understanding of the mechanisms of self-healing and the influence of the silicate constitution.

Keywords: rare-earth silicates, self-healing, water vapor corrosion

ABS 465

MICROSTRUCTURE, ELECTRICAL CONDUCTIVITY AND OXYGEN SENSING PROPERTIES OF ZIRCONIA BASED SOLID ELECTROLYTED, OBTAINED USING FREEZE-DRYING

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Due to the high conductivity, zirconia based ceramics is widely used as a solid electrolyte (SE) in the high temperature electrochemical devices, especially oxygen sensors. The working characteristics as well as the performance of oxygen sensors during their exploitation in the heated hazardous gaseous atmosphere or a melt significantly depend on the phase stability, electrical and mechanical properties of zirconia based SE. So the intensive work is performed nowadays to search the alternative SE compositions as well as new routes for the cost-effective manufacturing of zirconia ceramics with enhanced electrical and sensing properties. Thus the goal of the current work was the development of the novel scalable technique for the manufacturing of zirconia solid electrolytes with refined microstructure and enhanced properties.

Nanosized xCaO-(100-x)ZrO2 (CSZ, x = 9, 12, 15 mol.%) and 8Y2O3-92ZrO2 (YSZ) precursor powders were obtained by cryochemical technique including reversed co-precipitation and freeze-drying. Stabilized zirconia SE were synthesized from nanosized powders and annealing at 1823K in air for 3 hours. The comprehensive study of structure, conductivity of zirconia ceramics, obtained from freeze-dried nanopowders was performed by SEM (SEM, Hitachi S-3400N), XRD (Shimadzu XRD-6000, Cu K-alpha radiation, lambda = 1,54 angstrom) and impedance spectroscopy (Autolab PGSTAT 302N Potentiosytat/Galvanostat, quarz cell with Pt electrodes and contacts). Compression tests of cylindrical specimens were carried out according to the standard technique (dynamometer DOCM 3-5). Vickers hardness (HV) was determined at the load of 3 kg applied for 15 seconds (Shimadzu HMV-G21, diamond pyramid shaped indenter). EMF method was used for sensing properties measurement. The temperature was measured by Pt/Pt-10 %Rh thermocouple.

It was shown that the use of nanosized powders results in ceramics with refined microstructure. For different ceramic compositions a linear temperature dependence of conductivity is observed in range 523-973K, and ionic conductivity characterized by similar activation energies of conductivity. Using impedance spectroscopy it was proved that grain boundaries are thin and discontinuous. Via XRD and impedance spectroscopy it was shown that cryochemical approach is an effective and scalable way to manufacture cubic zirconia solid solution electrolytes having conductivity of ~10-1-10-2 Cm/cm at 1000K. Temperature dependencies of grain and grain boundary conductivity were obtained for all ceramic compositions. The mechanism of conductivity in CaO-ZrO2 was suggested. Sensors with YSZ, 9CSZ and 15 CSZ SE showed linear EMF response to relative oxygen partial pressure in all the investigated p(O2) range. The deviation from the theoretical value is minimal in case of sensor with 9CSZ SE. The suggested cryochemical technique can be scaled to various zirconia based systems. Work was supported by SPbSU grant.

Keywords: zirconia, solid electrolytes, oxygen sensors

ABS 453

WEAR MECHANISM OF SPARK PLASMA SINTERED MWCNTS REINFORCED ZIRCONIA COMPOSITES UNDER DRY SLIDING CONDITIONS

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Advanced ceramics composites have shown interesting tribological performances in a wide range of applications during the last decades. In the present work, the tribological properties of ZrO2 – 8 mol.% Y2O3 (8YSZ) containing (0 wt. %, 1 wt. %, 5 wt. % and 10 wt. %) of MWCNTs were investigated. The friction and wear rates were evaluated using the ball-on disk technique at dry sliding conditions. The sliding speed was set up from low (V1=0.036m/s) to high (V2=0.11m/s) values for comparative evaluation of the speed rate to the tribological properties of the studied composites. The microstructural examination after fractographic test revealed two types of fracture mode (trans-granular fracture and inter-granular fracture) depending on MWCNT content. The morphology of the wear tracks was visualized using Scanning Electron Microscopy. The factors responsible for achieving the highest wear rate in the monolithic material at low speed rate and significantly lower wear in the composites with MWCNTs have been determined. Finally, energy dispersive X-ray spectroscopy measurements were applied inside and outside the wear track to investigate the chemical composition of tribolayers accompanying the specific tribological properties obtained in our composites.

Keywords: Zirconia carbon nanotube, Wear mechanism, Tribological properties

ABS 447

COUPLED PHASE DIAGRAM EXPERIMENT AND THERMODYNAMIC MODELING OF THE Na2O-ZrO2 SYSTEM

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Na2O is a common constituent of conventional glass, and ZrO2 is the main material composing the refractory in glassmaking process. In order to investigate the corrosion of ZrO2 refractory in glass making process, the phase diagram information of the NaO2-SiO2-ZrO2 system is important. However, the phase diagram of the Na2O-ZrO2 system has not been well investigated yet. In the present study, the phase diagram of the Na2O-ZrO2 system was experimentally investigated by classical quenching technique as well as DSC thermal analysis. One congruent melting stoichiometric compound, Na2ZrO3, exists within the system. Based on the experimental data, thermodynamic optimization of the Na2O-ZrO2 system was carried out to present the complete phase diagram of the Na2O-ZrO2 system.

Keywords: Na2O-ZrO2,CALPHAD,Thermodynamic Modeling

ABS 445

AUTHIGENIC γ-Al$_2$O$_3$ FLAKE POWDERS FABRICATED USING THERMAL ASSISTED DELAMINATION OF BOEHMITE.

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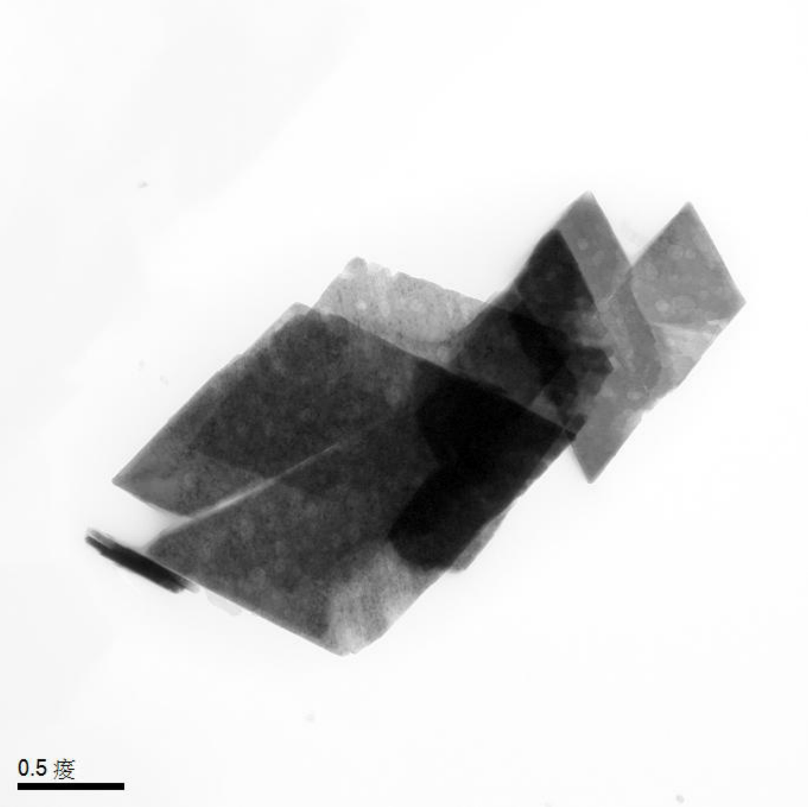
The topotactic transformation of boehmite (AlOOH) taking place under heat treatment that leading to forming γ-alumina (γ-Al2O3) has been conducted to fabricating authigenic γ-Al2O3 flake powders. This proposal is based on two major mechanisms. Firstly, the structural collapse of boehmite occurs, after hydrogen transfers and water extraction. Secondly, through an aluminum migration process, reforming the structure from layered ABAB.... to layered ABCABC....occurs. There can be involved the presences of the vapor pressure generated from dehydroxylation and the lattice strain from structure reformation between the layers. Based on the premise of generating γ-Al2O3, Differential thermal analysis (DTA) with five heating rates was employed to determine the endothermic detail of temperature ranges that induced by dehydroxylation, at the end of which γ-Al2O3 being formed. Calcined samples for examining delamination was then prepared with these five heating rates at the specific temperatures selected from the endothermic temperature ranges. The specific surface area (BET-N2) and the transmission electron microscopy (TEM) techniques were used to verify the delamination effect of each thermal treatments.

All γ-Al2O3 obtained at the temperature range between 525 degree Celsius and 640 degree Celsius with the five heating rates appear to have similar BET values and microstructure. However, the TEM analysis performed here reveals that the γ-Al2O3 particles obtained with slower heating rates may bring about an entire platelike morphology. While using a fast heating rate, it gives rise to the particle fragmentation.

By further simple mechanical processing on the calcined γ-Al2O3 obtained with slower heating rates, well delaminated γ-Al2O3 powders were achieved, confirming that the authigenic γ-Al2O3 flake powders can be fabricated using thermal assisted delamination of boehmite.

Keywords: <gamma>-Al2O3,flake powders, delamination process



ABS 436

STUDY OF TRANSFORMATION BANDS IN CERIA-STABILIZED ZIRCONIA-BASED COMPOSITES: DOES THE TRANSFORMATION-INDUCED PLASTICITY INDUCE DAMAGE?

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Due to their excellent mechanical properties, aesthetics and biocompatibility, Yttria-Stabilized Zirconia (Y-TZP) are of great interest in the biomedical field, especially in dental implantology. However, the Low Temperature Degradation (LTD) and moderate toughness of Y-TZP can affect its long-term viability in vivo. To overcome these issues, a new stable, tough and strong ceria-stabilized (Ce-TZP) zirconia-based composite has been developed. This composite with fine microstructure, high strength, full resistance to LTD and very high reliability also shows a significant strain to failure (near 1%) possibly related to transformation-induced plasticity (TRIP). Our goal within this study is to answer the question: is this elasto-plastic behaviour associated to transformation induced plasticity without damage?

Ce-TZP composite (84vol% $ZrO2$ with 11mol% $CeO2$, 8vol% $Al2O3$ and 8vol% $SrAl12O19$) provided by Doceram (Dortmund-Germany) was fully characterized. Load-unload tests were conducted in 4-point bending (4PB). The Young's modulus (E) was estimated from the slope of different load-unload loops and by Grindo-Sonic test (untested and 4PB-tested samples). Transformation bands were analysed by Raman spectroscopy in order to estimate the monoclinic (m) volume fraction. For microstructural observations, a thin foil was prepared by Focus Ion Beam (FIB) in order to be well-localized inside a transformation band. Then, Scanning and Transmission Electron Microscopy (SEM and TEM) observations were performed and coupled with Transmission Kikuchi Diffraction (TKD) analysis.

Tetragonal to monoclinic (t-m) zirconia phase transformation is visible in the shape of parallel bands after testing. During load-unload tests, the Young's modulus remained constant with subsequent cycles (E= 239 ± 7 GPa) and values were also very close to the one before the test and after fracture. This stability of the Young's modulus along the deformation and before and after 4PB-test could be related to the absence of damage. Microstructural characterization corroborated this conclusion since neither micro-cracks nor nano-cracks were observed inside the bands. The monoclinic transformed fraction was of 45% at the fracture zone and about 20 to 30% in other bands. Calculations suggest that shear component associated to the transformation should be much more important than the volume variation component. The volume fraction of monoclinic estimated from TKD mapping (15-20%) was in agreement with Raman results.

This study tends to show that developed Ce-TZP composites undergo transformation-induced-plasticity without damage, with a relatively low t-m transformation ratio. These results may re-open the discussion on ductile zirconia as an engineering material more than 40 years after the concept of "ceramic steel".

Keywords: Zirconia - Alumina, Composite - microstruture, Transformation - Plasticity

ABS 425

MECHANICAL AND TRIBOLOGICAL PROPERTIES OF DIRECT CURRENT AND HIGH POWER IMPULSE MAGNETRON SPUTTERED HiPIMS Hf-Zr-Ta-CONTAINING CARBIDE COATINGS

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High level of mechanical properties of the current hard multicomponent PVD coatings at temperatures well above 1000°C requires addition of one or several elements with high melting temperature [1]. They involve noble metals from IVB up to VIB groups of periodic table of elements, e.g. Hf, Zr, Nb, Ta, V, Ti, Y, etc. [1-2]. The, these coatings systems approach bulk multicomponent Ultra-High-Temperature Ceramics (UHTC) solid solution systems with high entropy [3-5]. The first coatings of this type were nitrides and carbides deposited by DC magnetron sputtering (TiZrNbHfTa)N and (TiZrNbHfTa)C [6] or by arc (TiZrNbAlYCr)N and (TiZrHfVNbTa)N, respectively, [7-8]. These works indicated that the reactive direct current magnetron sputtering (DCMS) is suitable for the formation of very hard coatings in these multicomponent high entropy systems. However, more recent High Power Impulse Magnetron Sputtering (HiPIMS) technique with higher level of ionization of sputtered species was not applied up to now. Therefore, the main scientific objectives of the work is the investigation of mechanical and tribological properties of HiPIMS deposited Hf-Zr-Ta-containing carbide coatings prepared by hybrid PVD/PECVD process and their comparison with the corresponding DCMS coatings. The deposition conditions will be optimized to obtain higher hardness and lower coefficient of friction via control of the hydrocarbon gas addition in the reactive atmosphere.

Acknowledgements

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Keywords: hard PVD coatings, HiPIMS, hardness

ABS 411

GAMMA RADIATION SHIELDING PROPERTIES OF REFRACTORY CONCRETE MATERIALS CONTAINING Ba-, Sr-, Fe-DOPED CEMENTS

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Objective

Due to the recent development of nuclear technology and use of technologies in various areas of industry, medicine and research, protection against high-energy ionizing radiation is one of the most important topics in this field. The exposure to radiation from X-rays and gamma rays causes several health effects as the result of absorption by the human . One of the most frequently used shielding materials for gamma rays is Pb. Despite the great effectiveness and high mass attenuation coefficient of lead, lower weight gamma shielding materials are required. Hence, concrete has been used in the construction of nuclear power plants because of three primary properties, its structural strength, its ability to shield radiation, and sufficiently long durability. Today, many research groups have wide interests in testing the strontium aluminates and barium aluminates-containing cementitious materials as hydraulic binders dedicated to radiation-shielding concrete.

Materials and Methods

In this work, the effectiveness of three composite ceramic materials based on mixtures of the Ba-, Sr- and Fe-doped phases belonging to the CaO-Al2O3-ZrO2 system, refractory aggregates and water was studied and compared with accepted values from the National Institute of Standards and Technology (NIST) database. The linear and mass attenuation coefficients of the materials were measured using variety of gamma quanta sources (152Eu, 22Na, 133Ba, 137Cs, and 60Co). This allowed to determine the energy dependence of the coefficients in a range of about 100 to 1500 keV. The measurements were performed with a High Purity Germanium detector providing excellent energy resolution and gamma quanta energy peaks separation. For each material the radiation intensity in a function of thickness and energy was determined which minimized the influence of systematic effects connected to the used method.

The structural and micro-structural properties of refractory concrete were characterized by XRD, FT-IR and SEM-EDS techniques. The thermal stability and dehydration mechanism of hydrated cement matrices were assessed by simultaneous thermal analysis TG-DSC-EGA-MS.

Results

The presented evaluation has shown that there is significant effect for the changes in the type of cement on shielding properties of concretes. The effects were also the structural and microstructural effects.

Conclusions

The presented work fits within the most significant current research trends of ceramic materials for shielding against penetrative gamma radiation.

Acknowledgements

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Keywords: shielding materials, gamma radiation, refractory concretes

ABS 410

MODIFICATION OF THE POROUS MULLITE CERAMIC WITH SOME METAL OXIDES

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The mullite ceramics can be used as a high-temperature thermal insulating material. These technical ceramics have such disadvantage as relatively low thermal shock resistance. The thermal properties of the mullite ceramics can be improved by the modification with metal oxides and additional phase compositions. The aim of the work is the investigation of the influence of stabilised zirconium dioxide and tungsten oxide on the structure and properties of the porous mullite ceramics, as well as the development of the heat-insulating thermal shock resistant highly porous mullite ceramic material.

Two types of commercial alumina (alpha and beta) with different particles size, pure silica oxide, kaolin, Al paste, tungsten oxide, yttria stabilised and magnesia stabilised zirconium dioxides were used as raw materials. The porous mullite ceramics were observed by the slip casting method of a concentrated suspension of raw materials. Porosity of the mullite ceramics obtained due to hydrogen gas evolution as a result of the reaction between Al and water. The sintering temperatures of the samples were 1500-1650°C, heating rate was 250°C/h and holding time at a maximum temperature was 1 h. Different parameters and properties of fired ceramics such as phase compositions, structure, chemical elements distributions, porosity, thermal and mechanical properties were investigated by corresponded equipment in the Institute of Silicate Materials.

The porosity of the samples with additives was about 63-73%. The presence of an aluminium tungstate phase with negative thermal expansion coefficient was observed in the samples. That decreased the thermal expansion behavior of the porous mullite ceramics in comparison with samples without metal oxide additives.

The usage of zirconium dioxide and tungsten oxide influences the phase compositions and structure of the samples, promotes the formation of the prismatic needle-like mullite crystals and decreases the mullite sintering temperature to 1600°C.

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Keywords: Mullite ceramic, Slip casting, Thermal expansion

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ABS 374

GRAPHENE NANOFILLERS/YTTRIUM-STABILIZED CUBIC ZIRCONIA COMPOSITES WITH ENHANCED THERMAL PERFORMANCE

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The evolution of the thermal diffusivity (α) and conductivity (κ) of yttrium-stabilized cubic zirconia (8YSZ) ceramics is studied for increasing additions (from 0 to 20 vol.%) of graphene nanoplatelets (GNP). These ceramic matrix composites with well dispersed graphene fillers are processed by mixing the initial suspensions of both components, i.e. graphene fillers and ceramic powders, and then drying and subsequent densifying using spark plasma sintering (SPS) technique. The α values of the composites are measured by the laser flash technique for specific orientations defined by the GNP alignment within the ceramic matrix -perpendicular and parallel to the SPS pressing axis. The thermal conductivity is, then, calculated from α data using the density and the specific heat of the materials. Results are comparatively discussed with thermal conductivity data previously reported by the for a group of ceramic/graphene composites showing a wide range of thermal conductivities, including ceramic matrices such as silicon carbide (SiC), silicon nitride (Si3N4) and aluminum nitride (AlN). In general, ceramic/graphene composites develop high thermal anisotropy because of the strong orientation of the graphene flakes when using pressure-assisted SPS process. In this way, the thermal conductivity of the composites is enhanced with increasing amounts of GNP in the direction defined by the graphene basal plane (i.e. perpendicularly to the pressing axis). Conversely, it is soundly impaired in the parallel direction for all composites, except for the 8YSZ-based one that showed strongly enhanced conductivity in both orientations, 100 and 750% for the perpendicular and parallel, respectively. In general, for increasing graphene filler contents, the ratio between the perpendicular and parallel conductivities rises within the range of ~2.0–4.0 for composites containing up to 20 vol.% of GNP. A resistance model consisting of series or parallel arrangements of the ceramic matrix and dispersed fillers for heat flowing in the parallel and perpendicular directions, respectively, is proposed to reproduce the thermal behavior of these ceramic composites. Especial mention deserves AlN composites as they experience a reduction of κ with the graphene addition for both orientations; actually the decrease of κ for the in-plane graphene orientation results rather unusual. This behavior has been modelled by introducing an interface thermal resistance in the effective media thermal conductivity models.

Keywords: thermal conductivity, graphene, zirconia

ABS 559

CORE-SHELL SOLID SOLUTION STRUCTURES TO ENHANCE HIGH TEMPERATURE PROPERTIES IN DUAL ZrB_2-$MoSi_2$ COMPOSITES

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An approach to escape from the classic strength-toughness trade-off in bulk ceramics using the dual composite architectural concept was explored and experimentally demonstrated. The reference system was ZrB2-MoSi2. Reinforcing granules dispersed in loose powder mixtures were hot-pressed, and fully dense dual composites were obtained. The role of solid solution shells in the densification behavior of ZrB2-MoSi2 composites was analyzed. The formation of core-shell solid solution structures in hot-pressed dual composites was confirmed by SEM, TEM and XRD analyses, and strongly affects the high temperature mechanical behavior. The brittle-to-ductile transition of MoSi2 above 1400 K enabled the simultaneous increase in both strength and toughness, and values of up to 440 MPa and 11.5 MPa-m½, respectively, were experimentally determined at 1773 K.

Keywords: zirconium diboride, molybdenum disilicide, mechanical properties

ABS 677

MECHANICAL PROPERTIES OF CERAMICS REINFORCED WITH ALLOTROPIC FORMS OF CARBON

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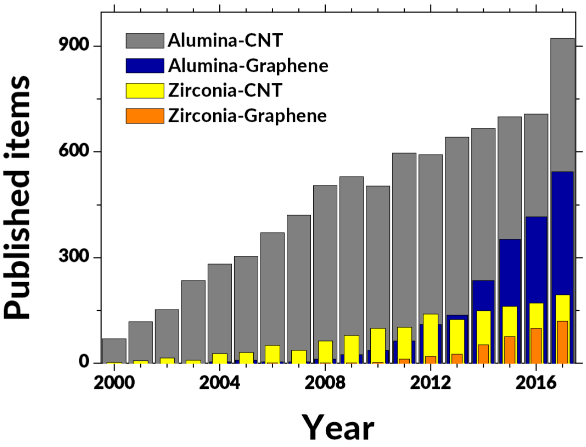
Since the discovering of the different carbon allotropes, carbon nanotubes (CNTs) and graphene have been considered as additives to overcome the brittleness of ceramics, and new Ceramic Matrix Composites (CMCs) were fabricated. Hence, these carbon allotropes have been introduced in a variety of polycrystalline ceramic matrix; among them, Al2O3 and YTZP are the most used in the industry. The figure shows the histograms of the publications concerning mechanical properties of these CMCs (ISI-WoK). This review will be focused on these two CMCs and the results on mechanical properties at low as well as at high temperatures. Special attention will be paid on the discrepancies regarding the different methods and results found in the literature.



Dispersion throughout the matrix is probably the most important requirement for reinforcement [1]. Regarding to this, graphene is preferable to CNTs because it does not form agglomerates in the matrix when it is treated appropriately. To obtain a good homogenization of the CNTs, several techniques have been used such as powder or colloidal processing. Nowadays, sol-gel technique has been also used to incorporate CNTs within alumina grains [2]. Regarding the mechanical properties at low temperature, hardness and fracture toughness are some of the most studied properties. The calculation of the fracture toughness usually involves Vickers indentation fracture and crack length measurements (in more than 80% of publications) since it eliminates the need for standardized samples and uses conventional hardness equipment and a small samples without pre-cracking elaboration. Besides, single-edged notched beam is also used, but similar results between both techniques have been reported for CMCs with low carbon content [3]. Nevertheless, different conclusions can be found such as significant toughening up to two-fold increase or no toughening and the debate about the reliability of fracture toughness measurements still remains opened. The results regarding the mechanical properties at high temperature point out grain boundary sliding as the deformation mechanism responsible of the behavior. In the case of the alumina, the main source of discrepancy is the existence of an extensive variety of alumina with a large dispersion in the diffusion kinetics processes and in the mechanical properties. Project P12-FQM-1079 (Junta de Andalucía) and V.M-F's grant (PPITUS-Universidad de Sevilla) are acknowledged.

[1] E. Zapata-Solvas et al. J Eur Ceram Soc 32 (2012) 3001–3020
[2] L. Esquivias et al. J Sol-Gel Sci Techn DOI:10.1007/s10971-018-4834-4
[3] M. Mazaheri et al. Comp Sci Tech 71 (2011) 939–45

Keywords: Reinforced ceramics, Carbon nanotubes, Graphene

ABS 363

SOL-GEL ALUMINA-GRAPHENE OXIDE CERAMIC MATRIX COMPOSITES

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The science of advanced ceramic has been developing different strategies in order to overcome the typical high brittleness of these materials that hinders their use in different applications. In particular, the reinforcement of alumina-based ceramic matrix composites (CMCs) have been pursued by the addition of carbon nanotubes or graphene as reinforcing phases [1,2]. Hence, mechanical properties such as hardness, fracture toughness or elastic modulus have been researched, looking for new advanced ceramics with reduced brittleness and enhanced mechanical performance. But, as a major rule, problems with the dispersion, the lack of a strong bond between the reinforcing phase and the matrix, and the location of the reinforcing phase on the grain boundaries (instead of a preferred intragranular location) have commonly impeded the achievement of incontestable and reproducible results [3,4].

We show alumina-based/graphene CMCs obtained by an original procedure based on the boehmite sol-gel route for alumina-CNT samples [5]. Its aim is to use the liquid-based sol-gel procedure targeting a good dispersion, the formation of strong bonds and the intragranular location of the graphene. In the figure, the precursor powder of the CMC can be seen, where a graphene nanosheet is wrapping the nanosized alumina particles that will subsequently form the CMC by Spark Plasma Sintering. A sample series with increasing graphene content has been synthesised, and their structural features have been characterized.

Afterwards, the mechanical performance have been studied in order to confirm its enhancement, paying special attention to the fracture toughness obtained by Vickers indentation and crack length observation. The relationship between changes in the mechanical properties and the graphene content have been discussed.

Project P12-FQM-1079 from Junta de Andalucía, P.R-A's PEJUS-2 grant and V.M-F's grant from Plan Propio Inv. (Universidad de Sevilla) are acknowledged.

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[4] M. Satam, L Gurnani, S Vishwanathe, A Mukhopadhyay, J Amer Ceram Soc 99 (2016) 2905-2908
[5] L Esquivias, P Rivero-Antúnez, C Zamora-Ledezma, A Domínguez-Rodríguez, V Morales-Flórez, J Sol-Gel Sci Techn Accepted. doi:10.1007/s10971-018-4834-4

Keywords: Alumina, Graphene, Sol-gel

ABS 361

EFFECT OF CARBON SUBSTITUTION ON MECHANICAL PROPERTIES OF TITANIUM CARBONITRIDE CERAMICS

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Transition metal carbides and nitrides are known to show excellent mechanical properties as well as exotic thermal properties, low electrical resistivities, extremely high melting points or good corrosion resistance. All these outstanding properties can be found in transition metal carbonitrides making them worthy of being studied.

This work is devoted to the analysis of the room-temperature mechanical properties of a particular example: Ti(C,N) polycristals. Monolithic titanium carbonitride bulk samples are first prepared by spark plasma sintering and then, microstructural and mechanically analyzed by means of X-ray diffractometry (together with Rietveld refinement), scanning and tramission-electron microscopies and indentation tests.

Fully dense specimens prepared at a peak temperature of 1800°C have been found to show excellent room temperature mechanical properties (23GPa Vickers hardness). A thorough discussion on the mechanisms involved in the mechanical response is also carried out.

Particular attention has been given to the microstructural changes produced during specimen consolidation as a function of the sintering atmosphere, finding a tiny improvent in sinterability. Finally, the effect of partial substitution of nitrogen atoms by carbon ones on the room temperature mechanical properties is discussed.

Keywords: Ti(C,N) ceramics, Spark Plasma Sintering, Hardness

ABS 358

INTRINSIC MECHANICAL PROPERTIES AND CONDUCTION MECHANISM OF FULLY-DENSE BORON CARBIDE CERAMICS AS A FUNCTION OF THE GRAIN SIZE

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A set of fully-dense boron carbide specimens was prepared by spark plasma sintering and grain size effects on their mechanical and electrical response were studied. In order to minimize residual porosity effect, nanoindentation tests were conducted under controlled displacement. It is the first time to our best knowledge that such study has been conducted. The tests show that hardness can reach values as high as 64 GPa. Nucleation of dislocations occurs when the local shear stresses are around 23 GPa, which is very close to the theoretical shear strength. Regarding electrical conductivity, DC conductivity was measured through four-point test technique from room temperature up to 800ºC. It was found that grain boundaries are structural defects reducing the conductivity controlled by bipolaron motion. The temperature dependence of the conductivity is controlled by the density of unblocked bipolarons. The temperature at which conductivity reaches the maximum value increases when the grain size decreases, which is consistent with theoretical predictions previously reported.

Keywords: Grain size dependence of B4C,Nanoindentation,Electrical conductivity

ABS 349

DEPOSITION OF CERMET COATINGS BY COLD SPRAYING AND ELECTROPLATING USED AS A REPLACEMENT OF HARD CHROME COATINGS

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Hard chrome coatings are widely applied in automotive and aerospace industry due to theirs anti-corrosion and anti-wear properties. Unfortunately, hexavalent Cr(VI) in the electrolytic baths is toxic and carcinogenic, and it is mandatory to find alternative materials and/or deposition technique in order to avoid this problem. The CerMet coatings appear as one of the most promising solution to that problem. A composite CerMet material, combining properties of ductile metal matrix and ceramic particles, should provide comparable results to the hard chrome coatings. The aim of this work is the application of CerMet coatings as a substitution of hard chrome.
In first group of samples titanium-based with carbides feedstock powder was used to obtain coatings by cold spraying, while the second group was prepared by electroplating from a nickel plating bath and carbide particles. The microstructure was analyzed using different characterization methods: X-ray diffraction, SEM. Dry sliding wear behavior and friction coefficients were evaluated via ball-on-disk wear tests at room temperature. The wear tests were conducted under different conditions, which allowed to create a wear map of the CerMet coatings.

Keywords: CerMet coatings, Cold Spraying, Tribology

ABS 347

SELF-HEALING Ni/Al$_2$O$_3$ NANOCOMPOSITES AS VERSATILE CERAMICS

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Al2O3 nanocomposites dispersed with nano-Ni particles (Ni/Al2O3) have been studied well as structural materials with high mechanical strength and high fracture toughness. Ni/Al2O3 also have thermal oxidation induced self-healing capability at high temperatures around 1200C in air. Self-healing of Ni/Al2O3 is caused by filling surface cracks with the oxidation product, NiAl2O4, which is formed with outward diffusion of cations. On the other hand, inward diffusion of oxide ions occurs to lead oxidation of nano-Ni particles in the inside of Al2O3 matrix. Diffusion properties in Al2O3 are very important for self-healing performance and oxidation resistance of Ni/Al2O3. Grain boundary doping of Al2O3 matrix is useful to control kinetics of self-healing and high temperature oxidation. As well, Ni/Al2O3 has possibility to show superplasticity at high temperatures. In this report, self-healing capability and high temperature oxidation of Ni/Al2O3 are described as well as production processes, mechanical properties and doping effects.

Keywords: alumina, nickel, diffusion

ABS 346

HIGH TEMPERATURE OXIDATION BEHAVIOUR OF Nb AND HfO_2 COATINGS ON ZrB_2

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ZrB2 has a unique combination of properties such as high melting point (>3000°C) and low theoretical density, high strength and elastic modulus which makes itself a very attractive candidate for ultra-high temperature applications. However, its' oxidation resistance is poor above 800°C which limits its application for aero-propulsion and hypersonic flight applications. Few studies have shown that the addition of transition metals into the ZrB2 material could improve the oxidation behaviour at high temperatures. In this study, two different materials were applied as oxidation protective coatings by means of magnetron sputtering technique on top of ZrB2 : the transition metal Nb and HfO2. The oxidation studies were performed at 1500 and 1600°C in a box furnace under synthetic air atmosphere for different times. Both coatings have shown promising results and the ZrO2 scale growth was drastically reduced. Formation of mixed oxides comprising of Nb and ZrO2 at the surface has reduced the oxygen transport at the ZrB2 reaction front. Similarly, HfO2 has acted as a barrier to the oxygen transport and a lower oxidation rate was achieved.

Keywords: UHTCs, Oxidation, Coatings

ABS 343

INORGANIC POLYMER MATRIX IN FIBER REINFORCED COMPOSITES

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For some years now, the need to develop new materials able to combine lightness, mechanical resistance and fire protection, possibly coupled with easy and sustainable processability, has been a key issue for different industrial fields. Especially in the automotive and aerospace industry, ensuring an optimal balance between performances and costs of the materials and allowing for a viable industrial scale-up and distribution are primary needs to assess.

To this aim, innovative fiber reinforced composite materials with properties and characteristics halfway between traditional FRPs and CMCs have been designed, in order to produce highly engineered complex geometry structures through a simple, sustainable and low cost process .

Such composite materials, based on a nanostructured fully inorganic polymer matrix, allow to achieve almost fully customizable properties and can be used for structural applications in the aeronautic, naval, rail field, replacing the most common materials as Inconel or Titanium superplastic alloy. Compared to conventional materials, they can boast interesting properties in terms of high temperature resistance (up to 1200 °C), no-smoke emissions, low thermal expansion coefficient (4*10-6 K-1), very low thermal conductivity (0.5 W/mK) and good mechanical properties (up to 200 MPa for tensile strength). Moreover, lightness and low life cycle costs make it a valid technological solution to replace heavy structural elements, especially when fire proofness and high working temperature are requested. Thanks to the possibility to easily realize complex shapes, the nanostructured carbon fiber material is an excellent candidate for the manufacturing of engine bay, engine exhausts, heat shields, nacelles, leading edges, nozzles and upper ducts of helicopters.

Keywords: Geopolymer, Nanostructured, Inorganic Polymer

ABS 336

TAILORING MICROSTRUCTURE AND INTERFACES FOR IMPROVED TOUGHNESS AND ABLATION RESISTANCE IN HfC CERAMICS

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Hafnium carbide (HfC) typically exhibits high melting point, high hardness and modulus, as well as excellent chemical and physical stability at ultra-high temperatures. However, associated with the intrinsic rigid covalent bonds, HfC is difficult to densify and show low toughness and plasticity, which limits its application as high-temperature structural materials.

By employing a nano-size carbon template and adjusting the content of a novel SiCN sintering aid, we have systematically tailored the microstructure and densification behavior of HfC materials prepared by the spark plasma sintering process. In addition to a significant enhancement of the final relative density (improved from 70% to ~97%), the fracture toughness measured by single-edge notched beam test increased largely from 3.8 to 8.4 MPa m1/2 while maintaining a sufficient flexural strength (520 MPa).

Based on the detailed microstructure and chemical analysis using Raman, XRD and multi-scale electron microscopy down to the atomic scale, the fundamental mechanisms for the observed enhancement on the density and fracture toughness are discussed. The key mechanisms are attributed to the unique microstructure of the obtained samples, which exhibits several important characteristics: 1) homogeneously dispersed SiC and C secondary phases in the HfC matrix; 2) HfC grains enriched with different levels of Si, O and N; and 3) fine grains with enrichment of C and O at grain boundaries. The microstructure led to beneficial chemistry and structure of several types of phases, phase boundaries and grain boundaries, which prohibit grain growth, facilitate mass transport and promote crack propagation resistance. The work can shed a light on rational microstructure design for optimum mechanical properties in high-temperature ceramics.

Reference:

1) W. Hao, N. Ni, F. Guo, F. Cao, J. Jiang, X. Zhao, P. Xiao, High fracture toughness of HfC through nanoscale templating and novel sintering aids, Journal of American Ceramic Society, 2018: 1-13*

Keywords: Hafnium carbide, Densification, Fracture toughness

ABS 329

DOPED ALUMINA SUBSTRATES FOR LASER INDUCED SELECTIVE METALLIZATION

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Laser induced selective activation and metallization is a novel fully additive metal plating process to deposit fine metallic conductor paths on alumina substrates. Complex three dimensional components shaped by ceramic injection molding (CIM) can thereby be equipped with electronic components and transferred into ceramic mechatronic integrated devices (MID).

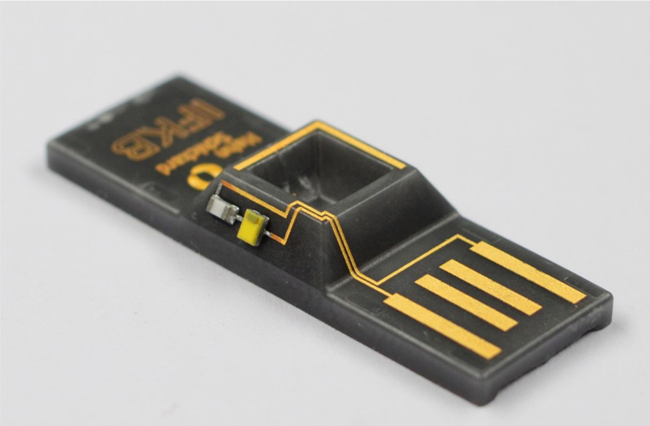
Hydrogen-sintered alumina has been identified as a reliable substrate material for the Laser Direct Structuring process. In this study the selective doping of alumina with various transition metal and rare earth oxides is investigated in order to produce laser activatable substrates by conventional sintering in air.

The oxide dopants in a concentration of 2 m% were introduced into an alumina slurry by mixing and milling. Slip cast samples were sintered at 1500°C in air and subsequently machined. Laser activation was performed on polished sample surfaces using a Nd:YVO4 laser with a wavelength of 532 nm and a pulse length of 10 ps under variation of selected laser parameters. Autocatalytic plating was carried out using commercially available copper electrolyte baths. Microstructure and mechanical properties, laser-matter interaction and metallization efficiency were investigated.

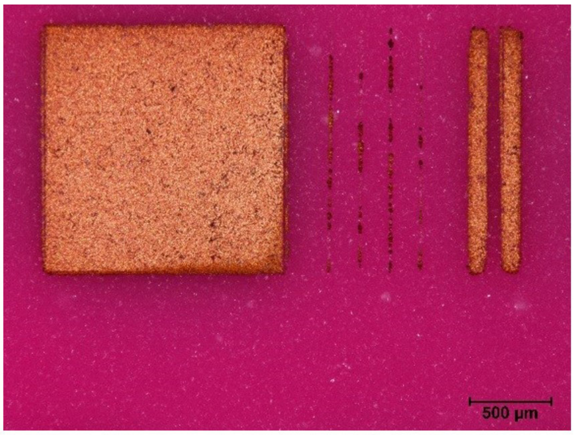
The study showed that rare earth dopants auch as Nd_2O_3 and Sm_2O_3 which lead to formation of monoaluminates or hexaaluminates were not suitable, the same result was found for CeO_2 and MnO. Transition metal dopants such as Fe_2O_3, NiO and Cr_2O_3 which for thermodynamic reasons can be suspected to form nanoscale lower valence oxide or even metallic nuclei at high temperature by irradiation with the laser were identified as suitable dopants which enable subsequent metallization.

NiO and Cr_2O_3 the most efficient dopants result in homogeneous and fine grain microstructure and similar strength and toughness as plain alumina. Other dopants may alter the alumina microstructure drastically by coarsening and precipitate formation, which not only affects laser activation but also strength and toughness.

Keywords: Alumina, Laser Direct Structuring, Doping



Ceramic MID demonstrator with hydrogen sintered alumina substrate



Selective metallization on doped alumina substrate sintered in air

ABS 321

FABRICATING TOUGHENED SUPER-HARD B_4C COMPOSITES AT LOWER TEMPERATURE BY TRANSIENT LIQUID-PHASE ASSISTED-SPARK PLASMA SINTERING WITH $MoSi_2$ ADDITIVES

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Toughened, super-hard B4C triplex-particulate composites were fabricated at lower temperatures by spark plasma sintering with MoSi2 additives (5, 10, and 15 vol.%). It is proved that MoSi2 is a reactive sintering additive that promotes densification by transient liquid-phase sintering, thus yielding fully-dense B4C-MoB2-SiC composites at ever lower temperatures. Specifically, it is demonstrated that MoSi2 first reacts at moderate temperatures (<1150 °C) with part of B4C thus forming MoB2, SiC, and Si. This latter is a transient compound that eventually melts (at ~1400 °C) contributing to densify by liquid-phase sintering, and then (at 1500-1700 °C) reacts with free C present in the B4C starting powders forming more SiC, moment from which densification continues by solid-state sintering. It is found that these B4C-MoB2-SiC composites are super-hard (~30 GPa), tough (~3-4 MPa · m½), and fine-grained, a combination that renders them very appealing for structural applications. Finally, research opportunities are discussed for the future microstructural design of a novel family of toughened, super-hard/super-hard multi-particulate composites based on B4C plus refractory borides and carbides.

Keywords: B4C,spark-plasma sintering, sintering additives

ABS 974

INNOVATIVE REFRACTORIES FOR IMPROVING THE EFFICIENCY OF INTENSIVE ENERGY SECTORS

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The use in industrial furnaces of new refractory solutions ensuring improved thermal insulation performance is expected to be beneficial in terms of energy saving toward more environmental-friendly processes, as well as increasing material life in service, which causes reduced use of raw materials and the consequent energy required for production. With this aim, different solutions have been explored. This work, carried out within the VULKANO project under financial support of the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 723803, describes the experimented solutions for laboratory production of the innovative refractories and the related results obtained by laboratory tests.

In particular, refractories were developed for withstanding the stressing operating conditions of the industrial sectors. The innovative refractories were produced first at lab scale and then at industrial scale (figures 1 and 2) with improved performance with respect to the currently used materials. The new developed refractories are to be used as technique validation in the demo sites (i.e., ceramic and steel sector).

For achieving these results, the following approach has been applied:

- market analysis for identifying the most suitable innovative components for refractories production;
- feasibility analysis of innovative refractories production using industrial by-products instead of expensive (and possible suffering shortage) raw materials;
- design and lab-scale realisation of two different refractory prototypes, with improved performances with respect to the currently used ones in the two demo sites;
- testing of the refractories produced at lab scale according to two optimized characterization protocols for the two demo sites;
- selection of refractory producers for industrial scale productions of the refractories;
- raw materials supplying and delivering for the industrial productions of the refractories to both demo sites (i.e., ceramic and steel sectors);
- investigation on the systematic feasibility of a production in an industrial scale;
- production of the best performing prototypes in industrial scale.

Figure 1. Refractory prototypes produced at industrial scale for validation at the demo site of the ceramic sector

Figure 2. Images of the platform lined with refractory prototypes installed in the steel sector demo plant.

ABS 973

EUTECTIC CERAMIC COMPOSITE FOR THERMAL BARRIER COATINGS

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There are a number of applications for ceramics that rely on their having low thermal conductivity at very high temperatures. Currently, the one of greatest impact on society is as a thin thermal insulation in gas turbines allowing coated single crystal superalloy blades and vanes to be used in gases whose temperatures exceeds the melting temperature of the alloys. Although a thermal barrier coating must also satisfy several other system and material requirements, its high temperature thermal conductivity is its primary characteristic. On the other hand, phase and microstructure stability at operation temperature is also the important issue for the durability and performance of thermal barrier coating (TBC) materials which have to work at high temperature for long time. In this work, we report eutectic system LaYbZr2O7 and LaYb(Zr1-xCex)2O7, which have thermodynamically stable fine-grained quasi-eutectoid structure with enhanced thermal insulation properties even under high temperature annealing. Their mechanical properties and thermal expansion property are also enhanced by the eutectic micro-structure. It will be a promising candidate for the next generation gas turbine.

Keywords:

ABS 297

INFLUENCE OF SINTERING METHOD ON PHASE COMPOSITION AND MECHANICAL PROPERTIES OF ZIRCONIA/ALUMINA/TUNGSTEN CARBIDE COMPOSITES

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Joining oxide and carbide phases in the one polycrystalline could be an effective method of significant improvement of mechanical properties of oxide structural materials. Mentioned connection sometimes results in the appearance of synergic effects very intensively increasing fracture toughness, strength and some useful properties of materials such as for example wear resistance. Common densification of oxide and carbide phases usually depends on the oxide phase sintering and carbide phase role could be described only as a grain growth inhibitor. Finally, carbide phase intensively hinder composite densification. Generally, it is difficult to densify oxide/carbide polycrystals using only the pressureless process. The sintering temperature increase could solve this problem but parallely it enable chemical reactions to proceed and decrease final properties of composites. Application of more intensive sintering techniques as hot-pressing (HP) or any field assisted sintering (FAST) allows to densify multiphase polycrystals at relatively lower temperatures. Moreover, decreasing of maximum temperature of the processing leads to significant grain size decrease. Both aspects strongly influence interphase (oxide/carbide) boundary properties and support very homogeneous residual stresses distribution in composites. This phenomenon change the way of cracking in the materials, support very significant fracture toughness increase and limits intensively wear susceptibility The paper describes mentioned phenomena in alumina/zirconia/tungsten composite carbide system.

Keywords: sintering, composites, microstructure

ABS 295

IMPROVEMENT IN SLAG RESISTANCE OF NO-CEMENT REFRACTORY CASTABLES BY MATRIX DESIGN

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The corrosion resistance of spinel-containing cement bonded castables has been extensively investigated in the past. However, corrosion of no-cement refractory castable (NCC) have not been widely studied since the use of NCCs has been relatively limited up till now. This paper compares the slag resistance of NCCs to a common spinel-containing low-cement castable (LCC). Three different NCC binders were designed: i) Al_2O_3+MgO; in-situ spinel formation, ii) Al_2O_3+SiO_2 (microsilica); mullite formation, and iii) Al_2O_3+MgO+ SiO_2 (microsilica).

Slag resistance trials were conducted using both the static crucible method and the rotary slag test. Two types of slag were used. The corrosion mechanisms were studied by means of Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and thermodynamic simulations of the corroded specimens. The results confirm that the chemistry of the slags and the mineral phases and microstructure of the refractory materials have strong impact on the corrosion resistance. The slag resistance was significantly improved when the cement was replaced by the cement-free binders.

Keywords: Corrsion resistance, cement-free castable, microsilica

ABS 279

OPTIMIZATION OF THERMOMECHANICAL PROPERTIES IN INVESTMENT CASTING SHELL MOLDS

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Objectives High-pressure turbine blades are essential components placed in the hot area of aircraft engines. After casting, blades can present irreparable defects caused directly by the refractory shell mold and ceramic/metal interactions at high temperature. Investment casting shell molds are layered structures made by successively dipping (wax models in ceramic slurry) and then stuccoing until the desired thickness is achieved, these layers generally have different compositions and grain sizes depending on their purpose in the system. By modifying external layers, the aim is to obtain structures resistant to thermal shock, hydrostatic pressure and creep, which can be also compliant during cooling; preventing residual stress in the metal at critical temperatures. Therefore, the main purpose of this study is to develop a new generation of investment casting shells that guarantee dimensional stability and metallurgical health of single crystal turbine blades.

Methods Shell samples (standard and new compositions) are studied by morphological methods at ambient temperature: scanning electron microscopy, energy dispersion spectroscopy, optical microscopy and x-ray diffraction; and by high temperature techniques: laser flash method, dilatometry, ultrasonic measurements, acoustic emission and high temperature tensile tests.

Results Thermomechanical properties (for example: young's modulus, expansion coefficient, thermal conductivity and diffusivity…), microstructural and phase evolution are determined throughout a cycle that mimics casting conditions. Investment casting shells exhibit mechanical strengthening at casting temperatures; as it occurs in most alumino-silicate mixtures, secondary mullitization might take place as a reaction between amorphous phases and alumina particles present in the structure. This rigidization might not be favorable for the metal in the beginning of solidification (before γ' precipitation in nickel-base superalloys). After a detailed analysis of previous studies and bibliographical review, new compositions have been proposed in an attempt to modify and control the final rigidity of shells, while still being resistant to creep.

Conclusions Tough temperature and pressure conditions during the casting require refractory shells to have a very specific behavior in order to obtain faultless metallic parts. This study shows the first steps towards an optimized shell mold composition with the desired thermomechanical properties that compromise both strength and compliance.

Keywords: Thermomechanical properties, Investment casting, Shell molds

ABS 277

SOLVING DAMAGE TO REFRACTORIES CAUSED BY THE BOUDOUARD REACTION IN CO/H2 ATMOSPHERE BY USING RAMAN SPECTROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY

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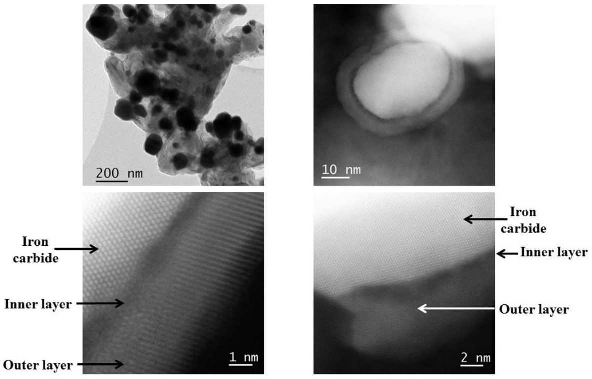
Refractory ceramics are very damaged by the Boudouard reaction catalysed by iron oxides.
The FexOy particles are transformed in the presence of CO into cementite by a carburation reaction, and the formation of carbon originates from a dissolution-precipitation mechanism.
Moreover, the addition of reducing gas H2 is known to drastically increase the amount of carbon.
The CO resistance of refractories is improved by the choice of raw materials with a low content of iron oxides and by the increase of sintering temperature. However, these solutions are not effective enough for new applications such as low- CO blast furnace process in which refractories are subjected to CO and H2 gas.
The aim of this presentation is to investigate the inhibition of the sp2 carbon formation in refractories catalysed by iron oxides under CO and H2.



Micrographs of the sample after TGA experiments exposed to 1000 ppm of SO$_{2(g)}$.
a) TEM image representative of the sample.
b), c), d) high-resolution HAADF-STEM images of a particle surrounded by a two-layer shell.

Thermogravimetric analysis was carried out on Fe2O3 samples exposed to a CO/H2 gas.
Solid sulphur was mixed with Fe2O3 powder or continually added in the form of gas into the CO/H2. The samples were characterized by X-ray diffraction, Raman spectroscopy, and TEM.
Sulphur is an efficient inhibitor to limit the carbon formation. From 100 ppm of SO2(g), the carbon growth rate decreases by a factor of 70 compared to an experiment without inhibitor.
A mechanism is proposed. With the addition of S, the iron oxide particles were reduced to cementite (Fe3C) and in Hägg iron carbide (Fe5C2). A nanometric FeS layer were formed around the iron carbide particles, preventing the catalytic effect of the Boudouard reaction.
Finally, practical solutions were applied to CO/H2 resistant refractories.
It is possible to control the structure, size and organization of the sp2 carbons produced by the Boudouard reaction. In the presence of a CO and H2 mixture, a carbon with a nano fibre morphology is favoured; with an addition of S, the catalytic effect of the iron oxide particles is prevented. This research opens the way to an effective solution to limit the damage of refractories.

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Keywords: Refractories, Boudouard reaction, Raman, Transmission electron

ABS 274

MICROSTRUCTURE AND TOUGHENING MECHANISMS IN ZIRCONIA COMPOSITES WITH DIFFERENT GRAPHENE-BASED NANOSTRUCTURES AND VARIOUS POWDER PROCESSING ROUTINES

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In this work, different powder processing routines to produce zirconia (3YTZP) composites with 1 and 5 vol% few layer graphene and graphene nanoplatelets (FLG and GNP, respectively) have been studied. The microstructure of the spark plasma sintered composites has been analyzed. In order to assess the integrity of the graphene-based nanostructures, their degree of dispersion in the ceramic matrix and the stabilization of the tetragonal phase in 3YTZP, Raman spectroscopy, scanning electron microscopy and X-ray diffraction have been used among other techniques. The hardness of the composites has been evaluated on the polished in-plane and cross-section surfaces, in order to account for any possible anisotropy, and correlated to the microstructure. The indentation imprints and indentation-induced fracture paths have been observed to identify the existing toughening mechanisms in these composites.

Keywords: Graphene-based nanostructures, Zirconia composites, Toughening mechanisms

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HIGH TEMPERATURE STABILITY IN OXYGEN AND HYDROGEN ENVIRONMENTS AND WEAR RESISTANCE OF Ti,Nb-Al-C MAX PHASES-BASED BULK MATERIALS AND VACUUM-ARC DEPOSITED FILMS

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MAX phases of Ti-Al-C system are the most examined and perspective for high temperature applications,they are light, electro conductive and demonstrate low friction characteristics, etc . But despite the combination of unique properties they did not find yet wide spread application (it is difficult to synthesize single phased material, they should combine a set of properties and even of singlephased materials can have very different characteristics because of synthesis parameters).
The bulk Ti2AlC, Ti3AlC2 and (Ti,Nb)3AlC2 developed by us are promising for the manufacture of interconnects of solid hydrogen fuel cells, pantograph, as damping substrates under the incisors, and others. The films Ti3.3-3.9AlC1.4-1.6 (5 μm thick) deposited on Ti using a vacuum-arc method from the target Ti2AlC (57 wt.%) +Ti3AlC2 (43 wt.%) were promising for high-temperature applications, in particular for interconnects fuel cells and as cavitation resistant coatings on turbines. After 1000 h heating at 600 oC the surface electrical resistance of the films only slightly decreased from 0.01 to 0,01-3 Ohm while the surface of pure Ti after 250 h in the same conditions totally oxidized and lost conductivity.
Investigation of the influence of H2 for 3 - 40 h and oxidation up to 1000 h at 600 oC, as well as thermocycling in air up to 600 oC on the bending strength and mass change of Ti3AlC2, (Ti,Nb)3AlC2, Ti2AlC showed that the highest absolute value demonstrated Ti2AlC and it was the most stable in the oxide medium (seems due to presence of some oxygen in the structure - Ti2,2AlC0,9O0,17). The bending strength of the Ti3AlC2 and (Ti,Nb)3AlC2 even increased after heating in H2. The addition of Nb allowed increasing the stability of the MAX phase in H2, and in air (the oxide film was twice thinner than that on the samples without Nb after 1000 h heating at 600 oC). The high temperature X-rays showed that Ti2AlC was oxidized more intensive than Ti3AlC2 at higher temperatures (Ti2AlC was stable up to 700- 750 ° C and Ti3AlC2 - up to 1050-1100 ° C). The most stable at thermal cycling to 1200 oC was a high-density material based on the MAX phase Ti3AlC2, obtained by two-stage technology (synthesis in vacuum with subsequent compression by hot pressing at 30 MPa). The oxidized layer of specimens contained ~100% of Ti3AlC2 but synthesized by one-stage hot pressing at 15-30 MPa for 10-30 min was twice thicker.
The wear of Ti3AlC2 materials obtained at 30 MPa according to the one- and two-stage technologies was very low (as compare to silumin), but the wear of the copper in contact with them was rather high. Significant reduction of wear of copper was achieved when the manufacturing pressure was reduced to 15 MPa: during friction in pair with copper its wear resistance in comparison with traditionally used silumin was 40 times higher, and the wear of copper was 14 times smaller (after 6 km of the way); Besides, Ti3AlC2 demonstrated much higher arc resistance.

Keywords: MAX phases, bulk and films, thermal and wear stubility

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HYDRATION BEHAVIOUR OF THE MgO-Al2O3 SYSTEM IN THE PRESENCE OF ORGANIC ACIDS UNDER HYDROTHERMAL CONDITIONS

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The refractory castables are widely used in metallurgical industry. The characteristic feature of this kind of materials is use of water as an essential component in production process. The use of water entails the risk of unwanted hydration process of basic components of the castables during preparation of castable mix as well as during heat treatment of the precast units and linings. There are numbers of substances (e.g. silica fume, ethylenediaminetetraacetic acid (EDTA), magnesium chloride ($MgCl_2$)) that influence on hydration reaction and allow to reduce or avoid negatives effects of this process. Among them hydroxy carboxylic acids are often considered as additives for refractory castables. The interactions between this substances and basic components of the castables is usually considered at room temperature under atmospheric pressure, while there is still lack of knowledge about the behavior of them in conditions, at elevated temperature and water vapor pressure, prevailing during firing precast castable units.

The aim of this work was to understand influence of hydroxy carboxylic acids on mixture of magnesium and aluminium oxides during hydrothermal treatment.

Study includes hydrothermal treatment at 240°C for 8 h the mixture of magnesium and aluminium oxides (1:1 molar ratio), with addition of citric and tartaric acid. The conditions of hydrothermal treatment reproduce conditions prevailing inside precast castables units during heat treatment. After hydrothermal treatment mixtures were tested using DTA-TG-EGA-MS, XRD and FT-MIR.

It was found that during hydrothermal treatment creates number of hydrated phases like brucite and boehmite and in case of samples with additives also double layered magnesium aluminium hydrooxide. Addition of citric as well as tartaric acid influences on the studied samples in similar way, and change the phase composition of the samples after hydrothermal treatment in reference to sample without additives.

Acknowledgements
This study was founded by The National Centre for Research and Development within the framework of LIDER VIII project No. LIDER/5/0034/L-8/16/NCBR/2017.

Keywords: spinel, castables, hydration

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HEAVY ION IRRADIATION DAMAGE IN Zr_2AlC MAX PHASE

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Zr-Al-C variations of the MAX phase family are potentially promising materials for components in future nuclear reactor systems. The capability of these materials will be limited by their behaviour under hostile reactor conditions: high irradiation damage and high temperatures. It is therefore encouraging that, in general, MAX phases have been shown to be remarkably resistant to damage when irradiated at high doses at high temperatures. However, no prior studies on the effects of irradiation on Zr MAX phases have been reported. In this study material containing the MAX phase Zr2AlC with 35 wt% ZrC as a secondary phase has been successfully synthesised. This material was then irradiated with swift Au ions. The irradiation was undertaken at room temperature, 300C and 600C. The damage acquired was estimated to be in the range 1-3.5 displacements per atom. These irradiated materials have then been characterised by transmission electron microscopy, scanning electron microscopy and X-ray diffraction techniques. Initial results suggest that both Zr2AlC and ZrC show little internal damage at these doses at 300C and 600C, while at room temperature there is clear evidence of amorphisation. In addition, microcracking is observed in the bulk material at 300C. For the range of temperatures and doses investigated, this phenomenon is independent of the irradiation dose.

Keywords: Irradiation, MAX Phase, Nuclear

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DEVELOPMENT OF CERAMIC SPRINGS FOR SENSOR APPLICATION

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At high temperatures and in harsh environments ceramic springs are often superior to metallic ones and allow for innovative solutions. A further application was proposed by using ceramic springs as capacitive force sensor. Lower and upper coil surfaces are coated by electrically conducting layers. Deformation of such spring results in a change of capacity. Sensor application calls for helical springs with rectangular cross-section, a linear stress-strain characteristic over entire deformation range and low manufacturing tolerances relating to inner and outer diameter, coil cross section and spring pitch. Furthermore, complex spring design with integrated connecting elements has to be realized.

Alumina, zirconia (Y-TZP) and silicon nitride springs were produced by hard machining starting from sintered hollow cylinders. After external and internal cylindrical grinding the hollow cylinders were filled with hard wax, followed by multi-stage cutting of spring coils with custom-made cutting discs. Finally, hard wax was removed by melting and burnout. Best surface and edge qualities of springs were reached using Y-TZP material and hot isostatic pressed alumina. Y-TZP springs produced with material-specifically selected cutting discs and optimized process parameters show sharp coil edges without spallings and mean roughness values of inner surfaces < 0.2 µm. Manufacturing tolerances of spring diameters, spring pitch, height and width of coil cross section are in the range of ± 10 microns. Good reproducibility of spring geometry by optimized hard machining technology allows for production of Y-TZP springs with spring constants differing less than ± 1 % within a series.

According to DIN 2090 spring constant for rectangular coil cross section is proportional to the square of height and width of coil cross section and indirectly proportional to number of active coils and to the cube of the mean spring diameter. Hence, spring constants can be tailored over a range of many orders of magnitude by changing the spring dimensions. Good agreement was reached between calculated target spring constants and measured values on produced springs.

Alumina and zirconia springs were characterized relating to deformation behavior under dynamic compression load with various deformation speeds and under static tensile loads over long periods of time. Contrary to alumina springs, a non-linear stress-strain behavior of TZP springs was proved in both test series. It is supposed, that pseudoelasticity caused by stress-induced transformation of tetragonal to monoclinic phase is responsible for this special feature of TZP springs. Therefore, TZP material cannot be used for capacitive spring sensors.

Keywords: ceramic springs, hard machining, deformation behavior

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IMPACT OF COMPOSITION CHANGE OF ALUMINA RICH SLAG ON THE CORROSION OF RAW MATERIALS USED IN STEEL MAKING REFRACTORIES

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In contact with corrosive medium (molten salts, molten oxides, fumes, gazes, and others), materials degrade. This is mainly due to chemical reactions which take place between the corrosive medium and the material. It leads to change in the microstructure and properties that usually decrease their performance. In general, refractories materials exhibit a better resistance to corrosion than other materials. That is why they are privileged to make steel ladle. This specific equipment for continuous casting is used to treat steel before casting. During the process a layer of slag floats on the steel to protect it and helps its treatment along by picking impurities. Due to this the composition of the slag changes from one process to another and during the treatment of the steel. These changes may impact the corrosion mechanisms and rate of bricks in contact with slag. The understanding of the corrosion behaviour of each raw materials composing the bricks can be valuable for a better understanding of the overall phenomenon.

To obtain a comprehensive analyses of corrosion of raw materials by alumina rich slags, different corrosion tests were realized: powder tests, contact tests and hot stage microscopy. The observation and determination of evolution of microstructure and phases composition were conducted by SEM and XRD. It helped to determine the impact of changes of slag composition.

The changes in slag composition can have a lesser or greater impact on the corrosion of the raw materials. One slag composition can be the more aggressive for one raw material and be the less aggressive for another one. The extend of the reaction that will take place will also be modified.

Corrosion tests between one raw material and one slag are interesting because it helps to determine the specific reactions that can happen between the two. However, in real conditions raw material are mix together to make bricks or concrete, hence experiment need to be pursued to see how the different effect of slag on different material will combine inside bricks.

Keywords: Corrosion, Slag, Raw material

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MECHANICAL BEHAVIOUR OF OXIDE-BASED CERAMIC MATRIX COMPOSITES AND DAMAGE ANALYSIS BY ACOUSTIC EMISSION

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Ceramic Matrix Composites (CMCs) are intended to be insert on new generation of civil aircraft engines. Their excellent thermomechanical properties and their low density suit to hot components requirements. In parallel of SiC-based CMCs, oxide-based CMCs are developed in order to replace metallic rear parts of the engine. The manufactory process – which is less expensive than SiC-based CMCs – generates several kinds of heterogeneities at different scales in the material (macroporosity, shrinkage cracks, microporosity…). The aim of this paper is to establish a relation between the microstructure and the mechanical behaviour of this new type of composite under tensile loading. In addition to macroscopic mechanical tests, damage mechanisms of this type of ceramic matrix composite is inspected through acoustic emission (AE) analysis and in-situ mechanical tests.

In this context, mechanical tests were realized on oxide-based CMCs with bi-dimensional weaving. Monotonic and cyclic tensile tests were performed at room temperature in two textile complementary orientations: tests in fiber orientation (0/90°) and ±45° regarding to textile orientation. The AE analysis is based on a signal approach using waveforms from four sensors (2 nano30 and 2 picoHF – MistrasGroup) with complementary frequency range. In order to establish a quantitative link between AE activity and damage mechanisms, X-ray synchrotron computed micro-tomography and SEM in-situ tensile tests were performed with AE monitoring. Localization of energetic signals in X-ray synchrotron in-situ tests match with important fiber-matrix debonding between bi-dimensional plies. SEM observations show lower scale damage (matrix cracks, small fiber debonding). Signal-based AE analysis coupled with in-situ tests, lead to a better understanding of the role of the microstructure on the damage behaviour, particularly the effects of delamination and the interactions between yarns inside the plies.

Keywords: Ceramic Matrix Composites, Mechanical Behaviour, Damage Mechanisms

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MWCNT INTRAGRANULAR REINFORCEMENT OF ALUMINA-BASED CERAMIC COMPOSITES PREPARED VIA SOL-GEL AND SPARK PLASMA SINTERING

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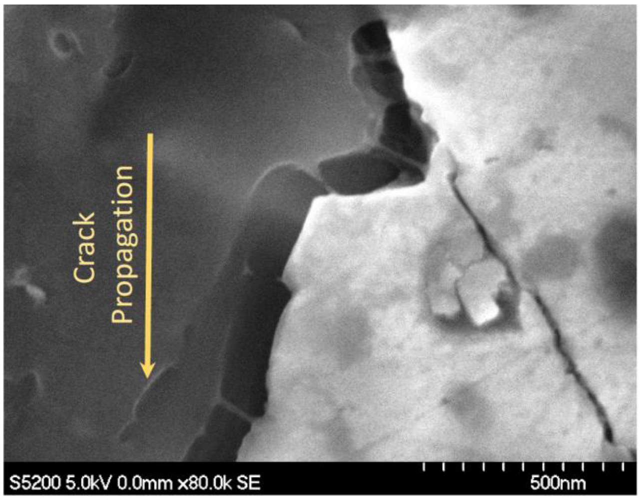
In the search for enhancing mechanical properties of Ceramic Matrix Composites (CMC), Multiwalled Carbon Nanotubes (MWCNT) were purposed as a promising reinforcement secondary phase. However, their typical location in grain boundaries questions the efficiency of this idea. In the frame of this problem, intragranular location of CNTs, appears as a solution to optimize the efficiency of CNTs as a reinforcer. With this goal in mind, Sol-Gel route was chosen as synthesis procedure [1], as it promotes the intergranular location of CNTs on the CMC [2-4]. A posterior rapid densification through Spark Plasma Sintering is used. This work presents structural and mechanical characterization at room temperature of sol-gel synthesized alumina-based composites with MWCNT, and explores the potentialities of the intragranular reinforcement of CMC.

Structural characterization has been carried out in a sample series increasing concentrations of MWCNTs, with techniques such as X-ray diffractometry, Scanning and Transmission Electron Microscopy, Nitrogen Physisorption and Thermogravimetry. The mechanical characterization has been performed by Vickers indentation and Berkovich Nanoindentation in order to study mechanical parameters such as hardness, fracture toughness or Young's modulus. After Vickers indentations, electron microscopy revealed that CNTs pull-out and bridging (see Fig.1) are involved reinforcement mechanisms. These effects, as well as the mechanical properties increase, are discussed.



(Caption: 'Figure 1. Fracture exhibiting bridging CNTs hindering crack propagation as toughness mechanism')

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Keywords: Sol-Gel Alumina, Carbon Nanotubes MWCNT, Intragranular

ABS 561

MECHANICAL PROPERTIES CHARACTERIZATION OF POLYCRYSTALLINE CERAMICS AT A LOCAL SCALE

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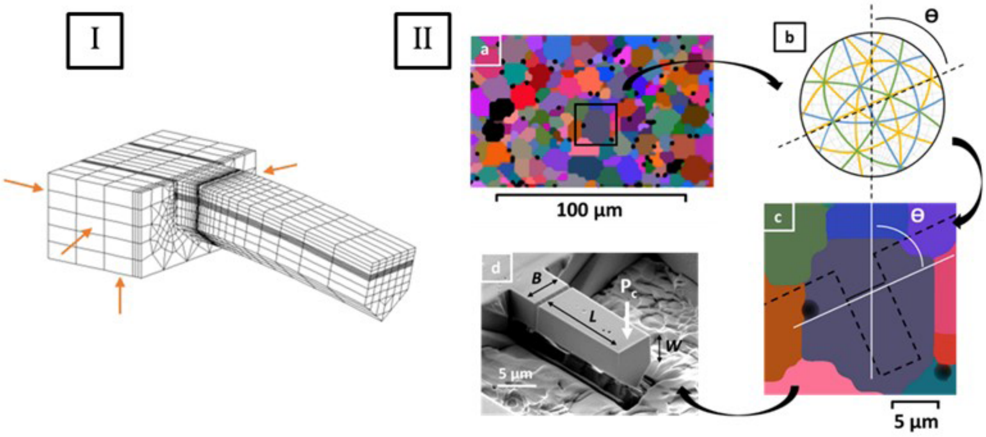
In the context of nuclear energy production, it is impossible to manufacture samples from irradiated uranium dioxide with a standard geometry for mechanical tests, because of micro-structural transformations (cracks, porosities…) induced by irradiation. However, mechanical properties such as fracture toughness are needed to feed numerical simulations for predicting the evolution of fuel pellets during their use. Therefore, we propose in this work to measure the local fracture properties of a polycrystalline ceramic through micro-bending tests on notched micro cantilever beams. In particular, the influence of crystallographic orientation on toughness was investigated.

Cubic zirconia with a micrometric grain size was chosen as a model material, because its crystalline structure is identical to the UO2 (Fm3m space group) and its fracture toughness for different crystalline orientations is known from macroscopic tests.

A finite element model of the test was first developed to calculate fracture properties for any beam design (see Figure I). This model was used to run parametric studies (check the influence of shape and dimensions of the beam, location of the notch …). Thanks to these studies, an optimization of the test parameters was performed. Then, beams of a few micrometers size were machined by a focused gallium ion beam in a SEM-FIB microscope, oriented along specific crystalline directions using EBSD measurements (see Figure II). Bending tests were then performed until fracture, the load being applied ex situ with a nano-indenter. The experimental load-displacement curves were finally coupled with the numerical model to calculate targeted mechanical properties.

The fracture toughness values obtained were compared to macroscopic ones. Finally, the influence of crystallographic orientations and of the beam parameters on fracture properties were discussed.

The approach followed in this work could be applied on irradiated nuclear fuel or on any architectured ceramic to estimate local fracture parameters (fracture stress, fracture toughness).



(I) Finite element model of the test, performed with Cast3m (CEA, Atomic Energy and Alternative Energies Commission). (II) Steps of the fabrication and orientation process: (a) Example of EBSD orientation map on cubic zirconia. (b) Stereographic projection in the SEM reference frame, attached to the grain with a black square in (a). (c) Schematic of the future cantilever contour with a notch position parallel to the targeted crystallographic plane. (d) Scanning electron microscopy image of the micro-cantilever beam obtained after FIB milling.

Keywords: Micromechanical testing, Toughness, Focused Ion Beam

ABS 230

A SIMPLE APPROACH TO BULK BIO-INSPIRED CERAMICS

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High strength and high toughness are usually mutually exclusive properties in structural materials. Resolving this contradiction is an important challenge for applications with a high demand for strong and damage-resistant materials. Bio-inspiration remains today an interesting approach to go through this conflict but the challenge lies on the lack of processing routes that allow a full control of the mutliscale structure organization and the fabrication of large samples with improved mechanical properties.

In this study, we present a simple process route to fabricate alumina-based ceramic composite with a multiscale architecture. This process is based on the alignment of alumina platelets during uniaxial pressing of field-assisted sintering in a spark plasma sintering (SPS) machine. The presence of glass precursors and alumina nanoparticles leads to the formation of a secondary glassy phase and mineral bridges between these platelets (Fig.1). This simple process permit to prepare large centimeter-sized samples and to test the size effect in crack propagation resistance curves. The presence of extrinsic reinforcement mechanisms (Fig.2) during crack propagation is confirmed, contributing to the damage-resistant behavior of these large samples, fabricated through a rather simple process.

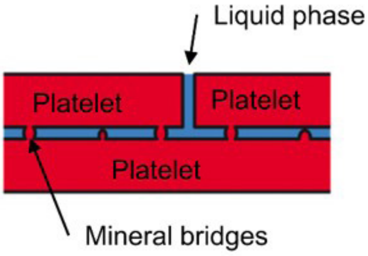

Fig.1 : Schematic representation of the multilevel structure

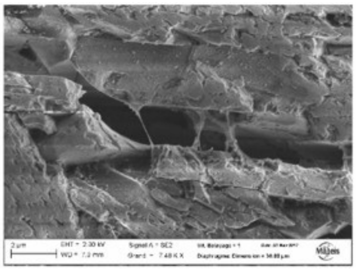

Fig.2 : Example of crack-opening at the interface between two platelets

Keywords: Bio-inspired ceramics, Toughness,SPS

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X-RAY TOMOGRAPHY CHARACTERIZATION OF PROCESSING DEFECTS IN ADDITIVELY MANUFACTURED ZIRCONIA: RELATION TO STRENGTH

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Additive manufacturing (AM) or 3D printing is currently developed for ceramic materials to avoid expensive machining, to obtain complex shapes or even to process shapes that could not be produced by other technologies. However, the reliability of AM ceramics is still a challenge that requires to clarify the interdependencies between their final properties and the processes. In particular, the characterization of the defects inherent to AM is crucial for the optimization of the mechanical properties.
In this work, X-ray computed tomography (XCT) analysis was applied to identify typical defects in YTZP zirconia processed by the Lithography-based Ceramic Manufacturing (LCM) technique. XCT derived strengths were determined from the XCT data and compared to experimental measurements. A good agreement between XCT data, bending strength measurement and fractographic analysis using Scanning Electron Microscopy demonstrates the suitability of X-ray tomography for both defects detection and predictive mechanical strength estimation.

Keywords: X-ray computed tomography, additive manufacturing, processing defects

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SACCHARIDE-BASED FEEDSTOCKS TO OBTAIN THERMAL BARRIER COATINGS BY AQUEOUS SUSPENSION PLASMA SPRAYING

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Thermal barrier coatings are used to protect metal parts from extreme working conditions, such as high temperatures and gas corrosion. Suspension plasma spraying (SPS) represents one of the most common methods of deposition since it is an inexpensive technique that allows to spray nanoparticles and microparticles and to obtain a wide variety of tailored microstructures. The microstructure of thermal barrier coatings plays a key role to improve mechanical and thermal properties. Many works have been addressed to optimize spraying conditions to engineer coating microstructure whereas feedstock suspension characteristics have been scarcely treated in literature.

In this work, an innovative design of thermal barrier coatings was carried out to improve the microstructure of the coating by modifying the properties of the aqueous feedstock suspensions. For this purpose, some common saccharides were added into aqueous suspensions of zirconia submicron-sized particles. The novel suspensions were characterized to determine the change produced by different saccharides through zeta potential, rheological behaviour, surface tension, and sedimentation rate for suspensions with 20 vol.% of solids content. The different suspensions were sprayed by suspension plasma spraying onto metallic substrates and the coatings were analyzed by scanning electron microscopy, X-ray diffraction and thermal conductivity was also measured.

Results revealed that the addition of saccharides only produced a slight change on suspension rheology, while significant impact on surface tension and sedimentation rate occurred. Thus, drastic changes of coating microstructures in terms of columnar structure development were attributed to this effect on liquid surface tension of feedstocks. These results showed that the use of saccharides can play an important role when designing the microstructure of SPS coatings.

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Keywords: Saccharides, Tailoring microstructure, Suspension plasma spraying

ABS 213

WC/W$_2$C COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS PROCESSED FROM W AND WC AQUEOUS SUSPENSIONS

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Cemented Carbides has a temperature limit of about 600ºC due to the presence of the cobalt based metallic phase. To Improve the thermo-mechanical behaviour and increase the use temperature and it has been proposed the substitution of cobalt by other refractory metals, such as Rhenium with allows higher working temperatures and pressures. On the other metals such as Nickel can improve the high temperature oxidation resistance of the compact.
This paper paper presented the fabrication of W2C/WC composite compacts by colloidal processing of WC and W powders in aqueous media to achieve ceramic metal composites with better mechanical response at high temperature, such as this required in nuclear technologies.

Aqueous processing of powders requires in-deep reactivity studies and the design of processing strategies to avoid the metal solubility and corrosion while keeping the dispersion forces of the powders in water. The conditions to chemically stabilize the powder in water are studied in terms of metal and ceramic dissolution at different pH´s showing that acidic conditions are required to avoid the tungsten dissolution as tungstate. The colloidal stability was determined in terms of the interparticles repulsion by determining the zeta potential of dispersions using Polyethyleneimine (PEI) as a cationic dispersants. It was found that dispersant has two effects on the slurries, one was to avoid the oxidation of the metallic tungsten in water in a higher pH range, and the other was the development of repulsions high enough to obtain slurries with solid contents as high as 20vol %.

Composites powders with different WC/W ratios were processed using slurries in the optimum dispersion conditions and following a controlled drying of the mixtures. The composite powders obtained showed a high and homogenous dispersion of the two phases that were characterized by SEM and XRD. After sintering by SPS at 1700° C with a pressure of 60MPa, the XRD analysis on cross sections showed the formation of tungsten carbide (WC) / Tungsten semi-carbide (W2C) composites. Mechanical properties measured by three point bending flexure strengths at 1200ºC as high as 1,2GPa can be achieved.

Keywords: Colloidal Powder Processing, Tungsten Carbide, Metal Ceramic

ABS 197

INTERACTION BETWEEN MATRIX COMPOSITION AND PROPERTIES OF SIC / SIC COMPOSITES

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Advanced ceramic matric composites (CMCs), in particular non-oxide CMC based on silicon carbide fibers and SiC matrices (SiC/SiC), are increasingly used for components in the hot gas path of advanced gas turbines in the aerospace and aircraft industry due to their excellent properties compared to traditional super alloys.
Besides a superior property level at ambient and elevated temperatures of the composites, the damage tolerance crack behavior is the most important requirement for these applications in aero engines preventing a catastrophic failure of the ceramic component during serve.

In the present study SiC/SiC composites were fabricated by a precursor infiltration and pyrolysis process (PIP). Fillers and additives can influence the properties of the composite materials and, in addition, reduce the number of infiltration cycles.
The composites were analyzed regarding their mechanical properties. Special emphasis was placed on the crack formation and propagation behavior in correlation to the microstructural features of the composites.
SiC / SiC composites with a 4PB strength > 500MPa and strain to failure >0.4 % were manufactured.
With the help of fillers and sintering additives and a subsequent sintering process, the structure of the matrix and thus the mechanical properties of the entire composite material can be strongly influenced. The fracture behavior can be adjusted between brittle to very good damage tolerance without additional fiber coating.

Keywords: SiC/SiC composites, matrix design, damage tolerant behavior

ABS 186

EXPERIMENTAL STUDY OF THERMOPHYSICAL PROPERTIES AND HIGH-TEMPERATURE BEHAVIOUR OF THE UHTC CARBIDES AND DIBORIDES UP TO 4500 K

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One of the essential points in the development of new UHTCs is their behavior at very high-temperatures. Since the melting temperature of some refractory carbides and diborides and their mixtures – the most promising materials for a very high temperature applications - are close to the domain of 4000 K investigation of their physical properties up to the maximum working temperatures is being a challenging issue. Sometimes one has to answer even the main question: how high is their melting temperatures? In order to shed some light on this latter topic one has to obtain precise data on phase diagrams of Me-C and Me-B2 systems as well as of some refractory mixed systems including high-temperature oxides.

The presentation is a review of novel original methods of high-temperature materials properties measurements developed recently at High Temperature Institute of RAS (Moscow, Russia).

The scope of the developments and investigations is related to extension of the temperature/pressure range of the co-called conventional thermophysics towards vicinity of the melting points of the most refractory substances. This goal is achieved using various laser heating experiments with the most refractory UHTCs. It is shown that different properties of UHTCs as well as graphite materials can be measured with a precision comparable with that of conventional commercial equipment. Laser heating methods are applied for measurements of different properties like high-temperature phase transitions [1], vaporisation and release studies [2], optical properties and thermal conductivity at temperatures up to ca. 4500 K.

Experimental results on solidus and liquidus lines in the Zr-C, Zr-U-C, Ta-Hf-C systems and TaC-C eutectic are presented. Thermal conductivity of ZrCx is studied for the various x within the homogeneity domain up to 3500 K. It turns out that for the all Zr/C ratios thermal conductivity is gradually increasing with temperature up to the vicinity of the solidus temperature however the absolute values are much depends on the composition and changing by factor of more than three over the solid solution domain. Thermal expansion measurements of ZrCx are also performed along with the thermal conductivity however the thermal expansion coefficient does not show appreciable dependence on the Zr/C ratio in the temperature domain of 2500-3500 K.

Spectral emissivity and even total emissivity measurements are performed in a very large temperature interval up to 4500 K.

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Keywords: Properties of UHTCs, Laser heating, Phase transitions

ABS 391

THE EFFECT OF GRAPHITE AND ZIRCONIA DISTRIBUTIONS ON THE TRIBOLOGICAL PROPERTIES OF PLASMA SPRAYED ALUMINA COATINGS

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To determine the tribological effects of graphite and zirconia distributions within a plasma sprayed alumina-coating matrix was the desideratum of this research.

Alumina with different weight percentages of graphite (5%, 10%) and zirconia (5%, 10%) were deposited on steel substrates by atmospheric plasma spraying (APS). To formulate the plasma, an air-hydrogen gas mixture was used. The coatings were produced at multiple torch powers. The surface morphology was inspected by a scanning electron microscope (SEM) Hitachi S-3400N. The elemental composition of the coatings was gauged by energy dispersive X-ray spectroscopy (EDS) Bruker Quad 5040 spectrometer. The surface roughness was computed using a Mitutoyo Surftest-SJ-210-Ver2.00 profilometer. Structural characterization of the coatings was done by X-ray diffractometry. Tribological properties of the samples were analyzed using a CETR-UMT-2 ball-on-disc tribometer.

With additive contents of graphite and zirconia, the surface roughness had increased from 2.75-2.82 μm and 2.82-3.62 μm, respectively. The surface morphology had rather a finer outlook with zirconia than graphite. XRD measurements indicated that the predominant phases in the alumina-graphite coatings were α-Al_2O_3 and β-Al_2O_3, and with alumina-zirconia coatings it was tetragonal: t-ZrO_2. The increase in torch power marginally changed the phase composition of the alumina-composite coatings.

The tribological properties of the alumina-composite coatings had been investigated to evaluate the friction coefficient and the wear-rate dependence on the type of additive powders and process parameters. The friction coefficient of the sprayed coatings was reduced with the addition of graphite. It was obtained that the wear rates of the coatings were in the range of ~10e-5 mm^3/Nm with certain exceptions pertaining to mere plastic deformations.

Keywords: Plasma Spraying, Tribology, Alumina Composite Coating, Additives, Graphite, Zirconia

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EFFECTS OF CRYSTAL STRUCTURE AND CATION SIZE ON MOLTEN SILICATE REACTIVITY WITH ENVIRONMENTAL BARRIER COATING MATERIALS

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Environmental barrier coatings (EBCs) are used to protect ceramic matrix composite (CMC) components from oxidation, corrosion, and detrimental interactions with molten calcium-magnesium-aluminum-silicates (CMAS) caused by ingestion of sand or volcanic ash in aircraft engines at temperatures above 1200°C. Rare-earth disilicate materials exhibit properties that are favorable for EBC application, although they corrode heavily when exposed to CMAS. The present study investigates the crystallization of various CMAS compositions with RE2Si2O7 (RE = Er, Dy, Gd, Nd) as a function of temperature and CaO/SiO2 ratios in CMAS systems. The change in cation species in coating material, as well as deposit chemistry, affected the amount of reaction products formed during interactions. These include the formation of a Ca2RE8(SiO4)6O2 apatite-type phase that is thought to form a boundary layer to prevent further infiltration of molten deposits in coating microstructures. Additionally, RE2Si2O7 crystal structure played a role in dissolution kinetics of the materials. Finally, conclusions are drawn between compositional changes of the apatite-type reaction product, changes in lattice structure, and consequences related to applying reactive crystallization of molten deposits to engine systems.

Keywords: environmental barrier coating, rare earth disilicate, CMAS

ABS 157

NANO-FUNCTIONALIZED CERAMIC FOAM FILTERS: EFFECT OF CARBON-BASED NANOMATERIALS ON WETTABILITY

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In this contribution, a novel suspension based on graphene oxide (GO) and multi-walled carbon nanotubes was prepared and applied on carbon-bonded ceramic foam filters. In comparison to reduced graphene, graphene oxide has much higher stability in water suspensions, hence it is more suitable for spray-coating. The rheology of suspensions containing GO, CNTs and a combination of both were analyzed and discussed. Xanthan proved to be a suitable stabilizer for all three systems. The spraying process of the suspensions was investigated with the aid of a high-speed camera. In addition, flat bulk substrates were also coated for investigations in contact with steel. The best results were obtained for the coating containing both GO and CNTs, since the sample surface was smooth and without cracks. Experiments were performed in a hot stage microscope to investigate the wetting behavior in relation to temperature and time. The microstructure of the substrates before and after heating was analyzed by scanning electron microscopy. For all temperatures, the measured wetting angle decreased with increasing testing time as expected. On the other hand, the sample treated at 1540 °C showed higher wetting angle (hence worse wetting) compared to samples treated at lower temperatures. This unique phenomenon may be attributed to the variation of the surface roughness due to the interaction between the functional coating and the steel drop. The results suggested that coatings based on 1D and 2D carbon-based nanomaterials may be useful to improve the purification effect of ceramic foam filters used in the steel industry.

Keywords: Ceramic foam filters, Graphene oxide, CNTs

ABS 155

MICROSTRUCTURAL INVESTIGATION OF FUNCTIONALLY GRADED ZrB_2-BASED ULTRA-HIGH TEMPERATURE CERAMICS

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One of the most promising materials for extreme temperatures in the UHTCs family is ZrB2, often in combination with 20-30 vol% SiC, which is known to improve mechanical properties and oxidation resistance. When SiC is added as fiber, it also notably improve the fracture toughness. Despite its good properties in aggressive environment, ZrB2-SiC materials show low sinterability, due to strong covalent bonds, and the operating temperature is limited to approx. 1650°C, since SiC severely suffers from active oxidation in the sub-scales. On the other side, MoSi2, with a high melting point, has been disclosed to promote densification and most of all it has been proven to positively affect the mechanical properties at high temperatures. However, when MoSi2 is combined with SiC fibers in a ZrB2 matrix and sintered above 1750°C, a progressive reaction of the SiC fibers occurs, with consequent degradation of the same. To preserve the beneficial effect of SiC fibers, the diffusion of Mo-compounds must be avoided. Therefore, a new concept of a Hf/SiCN-based thin buffer layer has been introduced, acting as a diffusion barrier to prevent the SiC fibers from MoSi2 attack. In this study, a layered structure of ZrB2-MoSi2 / buffer layer / ZrB2-SiCfiber-ZrSi2 was investigated, were the buffer layer is a ZrB2 powder encapsulated in a Hf/SiCN polymer-derived ceramic. After sintering, the material system has been oxidized in air for 15 min. at 1500°C and 1650°C. State-of-the-art scanning- and transmission electron microscopy (SEM/TEM) in combination with energy dispersive X-ray spectroscopy (EDS) are powerful tools to prove the functionality of the novel designed buffer layer. It sheds light on the existing phases and thus on ongoing diffusion processes. The effective functionality of the Hf/SiCN-based buffer layer has been proven by microstructural characterization. Molybdenum has not been found in- and below the buffer layer, whereas reference samples without a buffer layer revealed the overall presence of Mo, especially in the SiC fibers. Furthermore, it became apparent that the amount of available silicium has an influence on the severity of MoSi2 attack.

Keywords: Ultra-High Temperature Ceramic, Functional Graded Material, Short Fiber

ABS 150

NOBLE PROCESS FOR RECRYSTALLIZED SILICON CARBIDE THROUGH BETA TO ALPHA PHASE TRANSFORMATION

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Recrystallized silicon carbide is comparable to most refractory materials due to its high temperature stiffness, high resistance to thermal shock and outstanding corrosion resistance. In this study, a novel process for recrystallized silicon carbide through β-α phase transformation was investigated. The specimen prepared from carbon and β-SiC powder mixture was first infiltrated with silicon at 1500 degrees to form β-SiC preform with high density and then heated further up to 2200 degrees. When the β-SiC particles were transformed into α-SiC at 2200 degrees, the rapid grain growth of α-SiC occurred by consuming the β-SiC particles resulting in an interconnected network structure with huge elongated α-SiC grains. The measured density of the specimen heat treated at 2200 degrees was 2.7g/cm^3 and the strength of the specimen was 154MPa. The microstructures and properties of the recrystallized silicon carbide were examined and discussed.

Keywords: Recrystallized silicon carbide, Phase transformation, Density

ABS 140

THE INFLUENCE OF LOADING PROTOCOL ON THE DAMAGE DEVELOPMENT IN MECHANICAL FATIGUE TESTS ON SILICA REFRACTORIES

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Refractories serving in high temperature industrial units often fail due to repetitive thermo-mechanical loads. Mechanical fatigue tests allow analysis of the damage development due to cyclic loading. Herein we have investigated the failure process by performing cyclic fatigue tests of several methods. In uniaxial compression and three-point bending setups, we have loaded the specimens under stress-controlled and strain-controlled protocols. In the latter, we have applied the loading cycles with either constant displacement limits or constant displacement amplitude. Our cyclic fatigue analysis is supported by monotonic loading tests, non-destructive Resonant Frequency Damping Analysis (RFDA), DEM modelling and microstructural analysis. For the last, we have used light microscopy and X-ray micro-tomography techniques. We have found that the loading protocol significantly influences the potential to resist crack propagation. Depending on the protocol, the damage accumulation can be either sigmoid or exponential (saturation) function. The strain-controlled method allows more gradual, less brittle, failure than the stress-controlled method. The mechanical tests of various loading schedules can represent different service loads and assist in selecting the optimal refractory material.

Acknowledgment
The study has been put forward, on the possibility of studying the degradation of refractories due to thermal loads by mechanical tests, is a pre-study of a larger project. A more comprehensive study is underway within the ATHOR (Advanced THermomechanical multiscale mOdelling of Refractory linings) project framework. The ATHOR is a Marie Sklodowska-Curie Action European Training network – Innovative Training Network (ETN ITN) which has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement NO.764987.

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Keywords: Silica refractories,Cyclic fatigue,X-ray micro-tomography

ABS 139

OBSERVATION OF INTERNAL STRUCTURE OF Al_2O_3 CERAMICS BY OPTICAL COHERENCE TOMOGRAPHY AND ITS APPLICATION FOR NONDESTRUCTIVE INSPECTION

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Optical coherence tomography (OCT) is an observation technique utilizing optical interferometry. Images of the internal structure of opaque materials can be obtained dynamically and three-dimensionally in a few seconds. In this work, the internal structures of Al2O3 ceramics was observed by OCT. An artificially induced spherical defect having smaller than 50 µm in diameter which lies 700 µm below the top surface was observed successfully. Furthermore, the OCT observation was applied to nondestructive inspection. All coarse defects in the range of 1.5 mm of sample center were detected by OCT because they have possible cause of fracture. The strength was estimated by using OCT images and the Griffith equation. As the results, the estimated strength of 300MPa from OCT images well corresponded with the actual strength of 299MPa measured by three-point bending strength. In addition, the shape and size of fracture origin also agreed in the OCT image and the fracture surface image observed by SEM.

Keywords: optical coherence tomography, nondestructive test, internal structure observation

ABS 135

SILICON CARBIDE COATING OF 2.5D CARBON FIBERS BY CHEMICAL VAPOR INFILTRATION AND STUDIES OF OXIDATION BEHAVIOR IN THE PRESENCE OF RARE EARTH OXIDES

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Silicon carbide (SiC) coated carbon fibre preforms are important for the successful development and application of ceramic matrix composites as a continuous reinforcement phase. Selection of a suitable coating method for obtaining homogenous, dense and defect free SiC coatings on carbon fibres is crucial for obtaining superior mechanical and oxidation resistance properties. However, the use of SiC coating has the limitation of its poor oxidation resistance in the presence of moisture and/or over above 1600oC temperatures. To overcome these limitations, the addition of transition or rare earth metal oxides is being investigated with a view to improving the oxidation resistance by increased viscosity. The latter decreases the oxygen diffusion rate. Another potential benefit of increased viscosity, as well as increased liquidus temperature, is the suppression of silicon oxide evaporation from the glass. This work presents the chemical vapour infiltration (CVI) coating of SiC on 2.5D carbon fibre preforms and subsequent oxidation studies in the temperature range 1300 to 1700oC with or without rare earth oxides of CeO2 and Y2O3.
Thermogravimetric analysis (TGA) was used to study the continuous oxidation behaviour of pre-SiC coated carbon fibres up to 1400oC and the results compared to uncoated samples. Isothermal oxidation studies were carried out for SiC-coated samples in the temperature range from 1300 to 1700oC to understand the transformation from passive to active oxidation of the SiC & influence of rare earth oxides.

Important findings are:

i) Dense, homogenous and defect-free SiC coatings were obtained on 2.5D carbon fibres by the CVI method at temperatures of 1000oC.
ii) Continuous oxidation results indicated the SiC coating protected the carbon fibres from the oxidizing environment up to 1400oC by the formation of a continuous, crack-free and adherent SiO2 oxide layer. Carbon fibres in the preform that had remained uncoated were also protected from oxidation by the spreading of the glassy SiO2 layer over them.
iii) At 1300oC, the oxide layer completely covered all the carbon fibres with an oxide thickness of <1 μm.
iv) At 1500oC, the formation of cracks in the oxide layer was observed but the structural integrity of the coating was maintained.
v) At 1700oC the coating was completely degraded and subsequently lost shape and sustained an ~30 wt.% loss as the carbon fibres became exposed to the environment.
vi) Improved oxidation resistance was observed in the presence of the rare earth oxides.

Keywords: 2.5 D Carbon fibers,Silicon carbide,Rare earth oxides

ABS 125

CORROSION BEHAVIOUR OF SILICON NITRIDE AND SIALON IN MOLTEN FLINAK

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This work deals with the corrosion characteristics of liquid phase sintered silicon nitride and beta-SiAlON in the molten fluoride salt at the temperature of 600°C. After the corrosion test, the residual strength, weight change and depth of corrosion damage were investigated to estimate the corrosion mechanisms. The EDX and XRD analysis in different corrosion depth specified the development of different phases during corrosion tests. The experimental data were compared to the theoretical thermodynamic calculation in order to fully understand the corrosion behavior of the investigated materials.

Keywords: corrosion, silicon nitride, molten fluoride salt

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FRACTURE BEHAVIOR OF HIGHLY TRANSFORMABLE Ce-TZP / Al_2O_3 / HEXA-ALUMINATE COMPOSITES

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Zirconia based ceramics have proven to be successfully and widely used for biomedical applications due to their excellent mechanical properties, resulting from the stress induced tetragonal to monoclinic phase transformation occurring in this materials. Recent studies have shown that CeO2-stabilized tetragonal zirconia (Ce-TZP) based composites are promising for biomedical applications due to their high toughness and resistance to aging.

This work presents a study of the toughness and the R-curve measurements, under different testing methods, as well as of the slow crack growth (SCG) of a new developed bio-ceramic Ce-TZP/ 8vol% Al2O3/ 8vol% SrAl12O19. The composite exhibits different degrees of transformation toughening, obtained by varying the amount of the CeO2 stabilizer and the sintering temperature.

Toughness and R-curve are determined by single edge V notched beam (SEVNB) and double torsion (DT) methods. The SCG curves are determined experimentally, in air, under static loading by the double torsion method.

High fracture toughness values (up to 25 MPa.m1/2) are obtained with the DT compared to those of the SEVNB test, which is related to the R-curve behavior of the studied composites, strongly affected by the transformation rate and the loading configuration. Moreover, increasing the transformability of the composites increased their resistance to SCG, which is completely inhibited for the most transformable composites. All the composites show a high resistance to crack propagation compared to other developed bioceramics, demonstrating their capability to improve lifetime and reliability of ceramic implants.

Keywords: zirconia composites, slow crack growth ,fracture toughness

ABS 96

THE FORMATION OF Ta-Ir REFRACTORY INTERMETALLICS BY SOLID-STATE SYNTHESIS FROM TANTALUM AND TANTALUM CARBIDE

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Iridides of refractory metals (W, Hf, Ta, Mo, Nb etc.) are of great interest as ultra-high temperature materials due to the combination of properties of its components. These intermetallics were studied in the 60-70s of the past century as appropriate high-temperature structural materials for aerospace and aircraft applications, therefore, the phase equilibria in a great number of Ir-M systems (M = Hf, Ta, V, Nb, etc.) were thoroughly studied and described in several works. The formation of intermetallic compounds of different composition (primarily with the composition of MIr and MIr3) was found in most of the systems studied. However, the interaction of iridium with corresponding refractory carbides was studied poorly.

Recently, the interest in Ir-M intermetallics has been renewed due to the development of new generation of aircraft engines. Among Ir-based intermetallics, the tantalum-iridium system is of special interest due to high thermo-oxidative properties of tantalum.

The aim of this study was to investigate the mechanism of solid-state interaction of iridium with both tantalum and tantalum carbide at temperatures of 1000-1800°C. The solid-state interaction of Ir with Ta and TaC was performed by two techniques: (i) hot pressing of corresponding powder mixtures and (ii) heat-treatment of contact couples made up of Ir foil and Ta foil or sintered TaC disks at different temperatures. It was shown that the interaction of Ir and Ta metals leads to the formation of two layers of intermetallic products. The first layer of the variable elemental composition (25-60 at. % Ta) consists of a set of intermetallic phases and the second layer is TaIr3±x solid solution. During the TaC-Ir solid-state interaction, the only intermetallic product formed is TaIr3±x. It forms two sub-layers with different morphology. In addition, a free carbon phase is released. The Vickers microhardness of the obtained intermetallics was measured and turned out to be higher than that of pure Ir or Ta (top hard metals). The mechanisms of the solid-state reactions in the Ta-Ir and TaC-Ir systems will be discussed.

This work was supported by the Russian Science Foundation (Grant #18-19-00075).

Keywords: Tantalum Iridides, Iridium intermetallics, Solid-State Synthesis

ABS 75

SINTERING BEHAVIOUR AND OXIDATION RESISTANCE OF CARBON FIBRE REINFORCED ZrB2/SiC/WC COMPOSITES

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Reusable components for hypersonic flight, next generation rocket engines, and thermal protection systems require materials able to withstand extreme environments. The materials currently used in the aerospace field are based on C/SiC and C/C composites: the former can be used up to 1600°C due to SiC deomposition above 1600°C while the latter are ablative materials that can be used above 2000°C but are consumed in the process.

Ultra-high temperature ceramics (UHTCs), such as the borides and carbides of early transition metals having melting points above 3000°C are being investigated as a potential replacement for the fabrication of reusable materials. Among UHTCs, ZrB2 has been selected owing to its relatively low density. In order to improve the damage tolerance of UHTCs, fibre reinforcement was considered.

In the present work, the sintering behaviour, mechanical properties and oxidation resistance of carbon fibre reinforced ZrB2/SiC/WC composites was investigated. Sintering was carried out between 1800 and 2000°C via hot pressing at 40 MPa. The sample sintered at 1800°C is characterized by higher porosity, while the sample sintered at 2000°C is fully dense but fibres are severely degraded. A temperature of 1900°C allows to obtain 92% dense composite without excessively damaging the fibres.

The microstructure is characterized by the presence of ZrB2 and solid solutions of W-Si-B. Four-point flexural strength is in the range of 150-200 MPa, while fracture toughness is 4-6 MPam0.5. The sample sintered at 1800°C is characterized by higher KIc which was attributed to a higher degree of fibre pull-out due to weak fibre/matrix interface. The sample sintered at 2000°C is characterized by very strong fibre/matrix interface due to extensive reaction of the fibre with the surrounding ceramic matrix, leading to brittle fracture behaviour. A temperature of 1900°C was found as the best compromise to maximize strength and avoid brittle fracture. After exposure to 1650°C in air, three distinct oxide layers were identified: an outer silica layer, an intermediate layer constituted by columnar and needle-like ZrO2/WO3 grains and the unreacted matrix. Comparing the oxidation resistance with an un-doped ZrB2/SiC reference composite, the presence of WC leads to the formation of a more compact oxide scale, improving the oxidation resistance.

Keywords: UHTC, Carbon fibres, Oxidation resistance

ABS 73

THERMAL PROPERTIES CHARACTERIZATION OF INSULATING REFRACTORY MATERIALS USED IN STEEL LADLES

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The following research is part of a European project dedicated to “Advanced THermomechanical multiscale mOdelling of Refractory linings” (ATHOR), in the framework of the European Union’s Horizon 2020 Research and Innovation program, grant agreement number 764987. The main purpose of this work is to obtain a clear understanding of the high temperature heat transfer mechanisms taking place in thermally insulating refractory materials, which have complex microstructures, and to provide thermo-physical data for computer simulation studies of working refractory parts. Thermal properties play an important role in the performances of refractory materials in structures such as high temperature process vessels, furnaces.

Two methods (laser flash and hot wire/hot disk) are adopted to evaluate thermal diffusivity (α) and thermal conductivity (λ) of three kinds of insulating refractories: insulating boards, microporous silica sheets and fireclay bricks, the last two received via Tata Steel. These materials are used, in fact, in Iron & Steelmaking industries, in particular for steel ladle applications. Characterized by a very low thermal conductivity value, they constitute the insulation layer between the safety lining and the steel shell.

In ceramic materials, the intrinsic thermal conductivity for solid phases is determined by inelastic collisions and scattering of phonons. All the mechanisms that reduce the mean free path, such as phonon-phonon interactions or phonon scattering by defects, affect λ. The microstructure of a refractory material can also strongly modulate its thermal conductivity through the influence of pores and interfaces. For example, in a model material of fine grain alumina, the decrease of λ with increased porosity can be well described by Landauer’s relation for a two-phase mixture. The observed temperature dependence of thermal conductivity can be generally attributed to the predominance of either the solid or the porous phase. Another parameter to take into account is connected to the shaping process, which can yield preferential orientation of grains. For example, the insulating board’s anisotropy is related to different structural characteristics of grains in different directions. In particular, it is more insulating in the pressing direction, which is important as the material is used to reduce the heat losses through the lining.

Refractories are unique ceramic materials indispensable for high temperature processing. Essential key physical properties of refractories are the thermal properties, which are strongly connected to the microstructure. As they are multi-component materials, several parameters should be considered when analysing thermal properties. The influence of each parameter is not always well established.

Keywords: Thermal properties, Insulating materials, Steel ladles

ABS 59

MICROSTRUCTURE AND TRIBOLOGICAL BEHAVIORS OF SELF-LUBRICATING MESOCARBON MICROBEADS (MCMBs)-SIC COMPOSITE

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The solid lubricant being introduced into SiC matrix can effectively reduce the dry friction coefficient of SiC ceramics. In this paper, mesocarbon microbeads (MCMBs)-SiC composites were fabricated through hot-pressed sintering method at 2300K under argon atmosphere. The effect of sintering temperature and pressure on the densification of the composites was investigated. It was found that pre-pressing at 1200K could effectively improve the density of the composites. The microstructure of the composites was analyzed. It was found that the distribution of MCMBs was different in the directions parallel and perpendicular to hot pressing axis (HPA) due to the deformation of MCMBs under pressure. At the same time, according to electron backscatter diffraction (EBSD) analyze, in the direction perpendicular to HPA, the SiC grains were 4H crystal form and some grains prefered to be oriented along the crystallographic (0001) planes. However, in the direction parallel to HPA, the SiC grains were 6H crystal form and the grain orientation was discrete. The tribological behaviors of the composite under dry friction condition were characterized. It was found that the dry friction behaviors of the surface perpendicular to HPA were better than those of the surface parallel to HPA due to the different properties of lubricating film.

Keywords: MCMBs-SiC composite, Dry friction behaviors, Microstructure

ABS 40

CORROSION MECHANISMS OF MAGNESIA-CHROME REFRACTORIES IN COPPER SLAG AND CONCURRENT FORMATION OF HEXAVALENT CHROMIUM

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Magnesia-chrome refractories are essential materials for application as wear lining in copper production furnaces for many years. Formation of hexavalent chromium (Cr(VI)) has been a major concern despite its admirable corrosion resistance in copper slag. Magnesia-chrome refractory specimens (9, 12%, 15%, and 18 wt% Cr2O3) with addition of Al2O3 and TiO2 were fabricated and subsequent corrosion tests using copper slag was conducted in air. The corrosion mechanism between magnesia-chrome refractories fabricated and synthetic copper slag were investigated by means of X-ray diffraction (XRD) and scanning electron microscope (SEM), and concurrent formations of Cr(VI) were assessed effectively by the TRGS 613 standard Cr(VI) leaching test. All the magnesia-chrome specimens prepared are composed of periclase and composite spinel Mg(Al,Cr,Ti)2O4 phases after firing at 1700oC. Densification of the specimens decreases with the increase in Cr2O3 content due to the increased volume expansion, while TiO2 addition can improve their densification as mass transfer is enhanced during the sintering process. The corrosion resistance of the specimens decreases slightly with the Cr2O3 content due to the increased apparent porosity, which would result in penetration of more corrosive slag at the initial stage of the corrosion test while a newly formed (Mg,Cu)(Cr,Fe)2O4 spinel dense layer between the slag and penetration layer effectively hinders further penetration of slag and well protects the specimens. The Cr(VI) in the specimens prepared increases obviously with the Cr2O3 added content, while the TiO2 addition can suppress the formation of Cr(VI) effectively. Moreover, though the copper slag can cause the formed Cr(VI) to be reduced further during the corrosion process, concentrations of Cr(VI) in the leachates from TRGS 613 tests exceeded the European limit of 2 mg/kg in all specimens.

Keywords: magnesia-chrome refractories, corrosion resistance, Cr(VI) formation

ABS 14

HIGH ENTROPY B_2(HfMoTaTi)C AND SiC CERAMIC COMPOSITE

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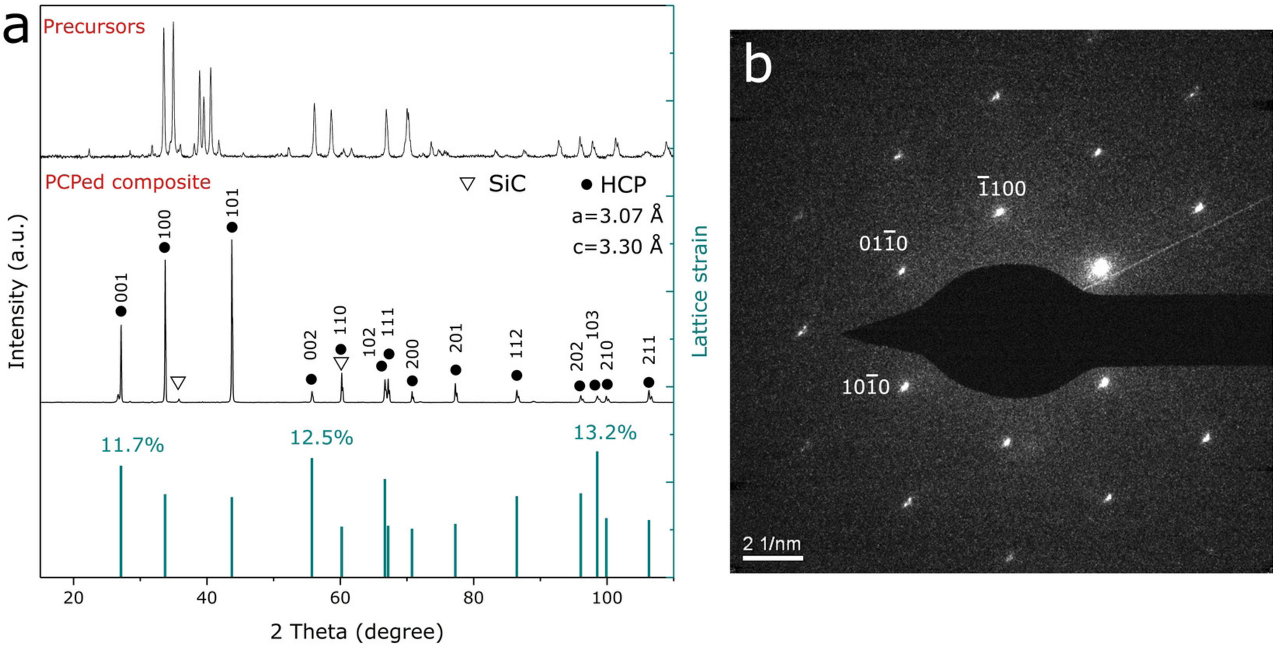
Refractory carbides HfC, Mo2C, TiC, TaC, B4C, and SiC were mixed with a molar ratio of 2:1:2:2:1:2 to fabricate multicomponent ceramic composite by pulsed current processing (PCP). From the starting materials that consist of face-centered cubic (FCC), hexagonal and rhombohedral crystal structures, the investigated carbide system is reported to form a single phase B2(HfMoTaTi)C high-entropy ceramic (HEC) with SiC. The HEC phase contains uniform distribution of constitutional elements Hf, Mo, Ta, Ti, B and C, according to Energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS) results.

The fabricated HEC phase displays a hexagonal close-packed (HCP) crystal structure, with a high average lattice distortion of 8.26% (see Figure). The HCP structure was observed by X-ray diffraction and selected area diffraction in transmission electron microscopy (TEM). Density-functional theory (DFT) optimization suggested that the hexagonal close-packed (HCP) crystal structure has alternating layers of metal atoms and carbon/boron atoms, i.e. metal atoms of Hf, Mo, Ta and Ti were distributed on the (0001) plane in the HCP lattice, while the carbon/boron atoms formed hexagonal 2D grids on the (0002) plane in the HCP unit cell. Despite of the vast differences in the crystal structures and lattice parameters among the utilized carbides, the formation of the unique hexagonal lattice structure of B2(HfMoTaTi)C can be a result of independent diffusion of the metal and nonmetal atoms. The sintered HEC ceramic composite exhibits excellent oxidation resistance at mediate temperature, 900 °C for 50h, and elevated temperature, 2000 °C for 20 s. Nanoindentation test shows that the HEC phase has a high hardness of 35 GPa. The remarkable improvement compared to the theoretical hardness value estimated based on the rule of mixtures (23 GPa) was contributed by the severe lattice distortion in the HCP structure.

Keywords: High-entropy ceramic, Ceramic composite



ABS 437

SYNTHESIS OF CONTINUOUS HAFNIA MODIFIED ALUMINOSILICA FIBERS BY MELT-SPINNING AND PYROLYSIS PROCESS

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Continuous HfO2-modified aluminosilica ceramic fibers with high Filament tensile strength and an average grain sized below 50nm were prepared by melt spinning process of a mixture of polymeric HfO2 precursor and aluminosilica precursor. The sintering parameters and recipe were optimized with respect to HfO2 precursor content, based on the influences on the average grain size, tensile strength and high temperature performance of the final ceramic fibers.

After1400 °C- 1 h treatment the grain size of HfO2-modified aluminosilica ceramic fibers were less than 100 nm, strength retention rates were about 60%. The results showed that HfO2-modified aluminosilica ceramic fibers can be used at an higher temperature calcination that contributed to the synchronized grain growth of both precursor-derived and HfO2 crystalline. The coarsening of alumina grain size could be restrained at high temperatures after introduction of a HfO2-forming constituent.

Keywords: Polymeric ceramic precursor, ceramic fiber, melt-spinning

S05

CERAMICS AND GLASSES FOR HEALTHCARE

INVITED LECTURES

ABS 966

BIOPHYSICAL STIMULATION OF STEM CELLS ON BIOCERAMICS AND IN BIOMICROFLUIDIC DEVICE: IN VITRO AND IN SILICO STUDIES

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Biomaterials science and biomedical engineering have sustained as one among frontier and growing areas of research and innovation within the engineering science community in the world; considering the number of scientific discoveries and their societal impact. Against the backdrop of the ever-increasing unmet clinical needs, significant efforts have been invested to innovate new bioengineering approaches for clinical applications. While introducing the fundamental concepts, it will be emphasized that the phenomenological interaction of a biological cell with a synthetic material is influenced by several factors, e.g. elastic stiffness, surface topography and wettability. In this context, the results of a strikingly different approach, involving the intermittent delivery of electric stimulation to manipulate cell functionality on electroconductive biomaterials will be discussed. I will present both the experimental results and theoretical foundation of our ongoing research in this direction. While establishing theoretical foundation to rationalize our experimental results, I will present the results of the analytical solutions of the Laplace equation with appropriate boundary conditions for the biological cell system, as well as MD simulation (GROMACS package) based studies for protein adsorption on biomaterial substrate and protein-membrane receptor interactions, both under the influence of electric field. This presentation, encompassing experimental results and theoretical analysis, is expected to provide guidelines to develop next generation biomaterials and biomedical devices for regenerative medicine.

Keywords: biophysical stimulation, bioceramics, biomicrofluidic device

ABS 797

MULTIFUNCTIONAL BIOACTIVE GLASSES RELEASING BIOLOGICALLY ACTIVE IONS: FROM BONE ENGINEERING TO WOUND HEALING

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In the last 20 years, bioactive glasses (BGs) have been widely used in tissue engineering approaches thank to their ability to bond to soft and hard tissues and to interact with target cells promoting new tissue growth. This presentation will cover the general field of bioactive glasses with ion releasing capability, with focus on recent developments in the field of MBGs incorporating ions such as silver and gallium. MBGs are characterized by large specific surface area, tunable and ordered mesoporosity with a pore size in the range of 2-50 nm and fast bioreactivity once in contact with biological fluids. These unique features make them optimal candidates to be used as controlled delivery systems of drugs, biomolecules and therapeutic metallic ions. The use of non-ionic surfactants such as Pluronic F127 as structure directing agent and the evaporation induced self-assembly (EISA) process will be described as effective approaches for the synthesis of MBGs. Silver and gallium were selected as therapeutic ions due to their well-known antibacterial properties and were introduced into the glass matrix during the synthesis process. In addition, sol-gel derived BG nanoparticles doped with therapeutic ions such as Zn, B, Li and Cu will be discussed, including their complete characterization by TEM, BET and bioactivity tests. Moreover, ICP-OES data will be presented to correlate the effective release of the selected ions with the biological activity of the MBGs, considering their interaction with target cells (e.g. osteoblasts) and their potential effect on angiogenic factors, e.g. of relevance for soft tissue repair and wound healing. The antibacterial capability of MBGs against Staphylococcus carnosus (Gram+) and Escherichia coli (Gram-) bacteria will be also presented. The results will show that MBGs are optimal candidates to be used as local delivery system of drugs, biomolecules, and therapeutic metallic ions, usually in combination with biopolymers (e.g. in electrospun fibres) or with 3D scaffolds fabricated from standard melt-derived BGs. Thanks to their unique mesoporous structure MBGs reduce the risk of possible dangerous side effects to the patient and exhibit an effective, controlled delivery of biomolecules and ions to exploit synergistic therapeutic effects.

Keywords: Bioactive glasses, Tissue Engineering, Ion and drug delivery

ABS 737

FORTY YEARS AFTER 'CERAMIC STEEL' ? THE ANSWER OF CURRENT ZIRCONIA CERAMICS TO THE REQUESTS OF THE DENTAL COMMUNITY

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40 years ago, Garvie and co-workers reported that the transformation of metastable tetragonal zirconia grains towards the monoclinic symmetry could give rise to a powerful strengthening mechanism. This led them to consider zirconia systems as analogues of certain steels. This seminal paper generated extraordinary excitement in the ceramic community and is still the subject of extensive research. On a practical point of view, zirconia finds applications in numerous fields and most recently for biomedical devices. In particular, the use of zirconia ceramics in dentistry has shown an unprecedented evolution this past decade, thanks to their specific properties, with potential high strength and toughness, associated to color and translucency (for some compositions). For example, 'monolithic zirconia' restorations, for which thick glass-ceramic veneers are no more mandatory, are a real buzz in the dental community. Zirconia dental implants are also proposed as a serious alternative to titanium by several companies.

In the field of dental restoration, a wide range of compositions are today proposed, with the addition of alumina to improve aging resistance or with more yttria to improve translucency. In all cases, there is always a compromise between aesthetics (translucency and color), mechanical resistance (related to the potential of transformation toughening) and long-term stability (aging resistance). Playing with this trade-off is a current source of research and shows that there is not 'one zirconia' but a range of zirconia ceramics with different features. In that sense, the term 'ceramic steel' is well adapted because of the similarity with the 'steel family'. Here, we will therefore describe the different 'zirconia' ceramics that can be found on the market and in our research strategy.

Zirconia also exhibits several interests for dental implants. Without being exhaustive: (i) zirconia does not lead to corrosion or ion release, (ii) it has good affinity with soft and hard tissues, (iii) it exhibits sufficient toughness for most dental implant applications. On the other side, we must not forget the balance between a good osseointegration generally improved by surface modifications and the need of sufficient strength and aging resistance (which might be compromised by surface modifications). If 3Y-TZP is currently and obviously the zirconia of choice for the fabrication of implants, we will describe shortly (as it will be the focus of other talks from our team) the alternative development of ceria-doped zirconia based composites, which exhibit high toughness, high defect tolerance and high aging resistance.

Keywords: zirconia, dental restorations, dental implants

ABS 964

BIO-INSPIRED CALCIUM PHOSPHATE APATITES: BIOMEDICAL PROMISES BEYOND BONE REPAIR?

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Bone is a natural nanocomposite with an exceptional reactivity. Its mineral component is composed of nanocrystalline apatite. Mastering the synthesis, physicochemical and thermodynamic characteristics of synthetic “biomimetic” apatites resembling bone mineral thus allows exploiting their intrinsic biocompatibility, nanoscale dimensions, and high surface reactivity to develop, beyond bone applications, also uses in other fields like nanomedicine. We have previously demonstrated that such apatites could be elaborated in the form of colloidal nanoparticles (NPs) upon stabilization with an organic corona, and in vitro tests revealed their low cytotoxicity and non-proinflammatory potential 1. The addition of additional functions such as antibacterialness, luminescence and cell targeting was also shown to be feasible, thus widening the potential domain of applications of such stabilized NPs. After a general presentation of biomimetic apatite-based NPs, we will present here mainly our recent progress in the use of these NPs for hematology and dermatology. Our findings demonstrate that colloidal nanocrystalline apatite-based particles are innovative systems able to interact with cells and tissues, which we will illustrate with the examples of Red Blood Cells cryopreservation and the development of a multifunctional dermatological gel. Complementary data on the hemocompatibility of such NPs as well as their interaction with cell membranes and artificial phospholipid bilayers will also be presented. Appealing new applications can be expected for such bio-inspired colloidal apatite particles, even beyond bone repair…

References

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Keywords: Colloidal nanoparticles, Bio-inspired apatites, Nanomedicine

ABS 615

IN VIVO AND IN VITRO DEGRADATION OF CALCIUM PHOSPHATES: EFFECT OF MULTISCALE POROSITY, TEXTURAL PROPERTIES AND COMPOSITION

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Introduction Synchronisation between biomaterial degradation and bone formation is a crucial issue when designing synthetic bone grafts. The active degradation of synthetic bone grafts in vivo results from the dissolution of the material in the acidic environment produced by bone-resorbing cells. Therefore, their degradability depends not only on composition and textural properties, like porosity and specific surface area (SSA), but also on the inflammatory reaction and the osteoclastogenesis elicited by the material once implanted. This study aims to evaluate the effect of composition, SSA and porosity at various length scales, on the in vivo degradation of different calcium phosphates. Moreover, to better understand the interplay between chemical and biological phenomena, the results were compared with the in vitro accelerated degradation of the same scaffolds.

Materials and Methods Calcium deficient hydroxyapatite (CDHA) scaffolds with different pore architectures were obtained by: i) Foaming and hydrolysis of an alpha-tricalcium phosphate (a-TCP) slurry (CDHA-Foam); or ii) robocasting of a self-setting a-TCP ink (CDHA-Rob). Two different nanostructures, fine needle-like crystals (F) or coarse plate-like crystals (C) were obtained by using either fine or coarse a-TCP powders respectively. Carbonated CDHA foams were obtained by hydrolysing a-TCP in a sodium bicarbonate solution. Sintered beta-TCP was used as control. Scaffolds were characterized in terms of composition, porosity, solubility and microstructure. The in vivo study was carried out in a standardized model of intramuscular and intraosseous implantation over 6 and 12 weeks in beagle dogs. Material resorption was evaluated by micro-CT. The susceptibility of the material to acidic degradation in vitro was assessed by immersing the samples in an acidic solution at 37 °C to mimic the osteoclastic environment.

Results and Discussion Similar degradation trends were found intramuscular and intraosseously, although the absolute values were higher intramuscularly. Carbonated CDHA-Foams exhibited the highest degradation rate, followed by the CDHA-F-Foams, above b-TCP at 6 weeks and similar to it at 12 weeks, and finally by CDHA-C-Foams. This evidenced the importance of textural properties, which modulated or even outweighed the effect of intrinsic properties such as solubility. Pore architecture played a significant role on degradation, CDHA foams showing a significantly higher degradation than robocast counterparts. Interestingly, in vivo degradation was not fully consistent with the degradation results in vitro. Thus, whereas CDHA-F-Foam, with the highest SSA, showed the highest degradation rate, exceeding the more soluble b-TCP, the incorporation of carbonate in CDHA rather than increasing the in vitro degradation, significantly reduced it.

Acknowledgements

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Keywords: Scaffold, degradation, in vivo and in vitro

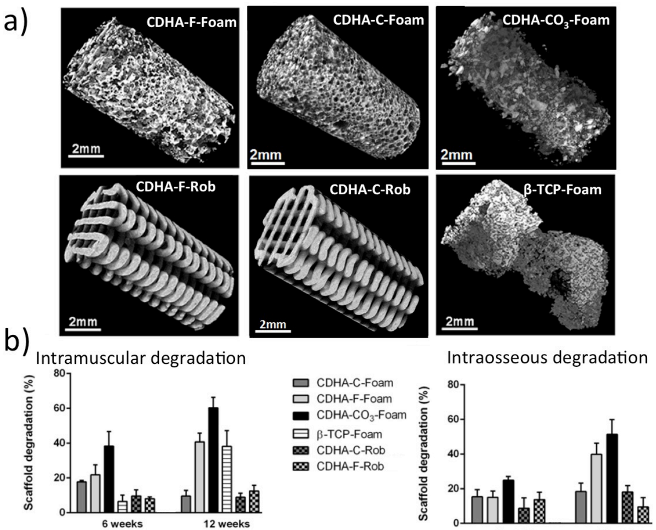

Figure 1. a) Micro-CT 3D reconstructions of the studied scaffolds 12 weeks after intramuscular implantation; b) Quantification of scaffold degradation after intramuscular and intraosseous implantation

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IN VIVO EVALUATION OF 3-D PRINTED BIOACTIVE APATITE CONTAINING GLASS CERAMICS

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The paper presented here deals with the investigations of apatite containing glass ceramics (AP40mod, BAM, Berlin, patent family WO 2014/146831 A1) of the chemical composition (wt%) 39.60 SiO2, 32.04 CaO, 11.26 P2O5, 2.01 Na2O, 3.52 MgO, 5.03 CaF2, and 6.54 TiO2 for the use in 3D printing and DLP lithography in order to create porous, bioactive, loadbearing bone replacement scaffolds.

The inhouse produced ceramics where crushed and sieved to achieve particles of irregular shape in the size ranges of 45-100 µm and 25-45 µm, respectively, for 3D printing (3DP) and below 25 µm for DLP lithography. Cylindrical shaped samples (tablets of about 10 mm diameter and 3 mm thickness) and custom-made scaffolds where printed by powder bed 3DP and DLP lithography respectively. It was found that 3DP samples could be resorbed in vivo within 24 weeks almost completely while DLP processed samples do not. It is assumed that the solubility of AP40mod is related to porosity, density and accsessible surface area. This observation would allow adaption of the resorbability of the glass ceramic scaffolds in a wide range by the macro- and microstructure of the 3D printed samples.

Keywords: glass ceramics,3D printing, DLP lithography

ABS 345

TWO PHOTON POLYMERIZATION-BASED ADDITIVE MANUFACTURING OF MEDICAL DEVICES AND PROSTHESES

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We have used an additive manufacturing process known as two photon polymerization to create microneedles and other microstructured medical devices. The two photon polymerization process involves spatial and temporal overlap of photons, resulting in photo-polymerization within well-defined and highly-localized volumes. The desired three-dimensional microstructured medical device is created by polymerizing the material along the laser trace, which is moved using a microscale positioning system. Two photon polymerization provides many advantages over conventional methods for scalable processing of microstructured medical devices. Many types of inexpensive hybrid materials, polymers, and other photosensitive materials may be processed using two photon polymerization. Two photon polymerization can be conducted in a conventional manufacturing environment that does not contain cleanroom facilities. Finally, two photon polymerization of microstructured medical devices is a straightforward single-step process, as opposed to conventional multiple-step processes.

Ossicular replacement prostheses were produced by two photon polymerization of hybrid materials. The Irgacure® 369 initiator (Ciba Specialty Chemicals, Basel, Switzerland) typically used for two photon polymerization has an absorption peak at around 320 nm. Femtosecond laser pulses from a titanium: sapphire laser were used for processing the photosensitive resin.

Two photon polymerization was able to create microneedles with a larger range of sizes, shapes, materials, and material properties than conventional stainless steel or titanium microfabrication techniques. A microneedle array was created out of a hybrid material on a glass substrate using two photon polymerization. The flexibility of the two photon polymerization process allows rapid processing of microneedles with various designs. In-plane hollow microneedle arrays and out-of-plane hollow microneedle arrays in various geometries were prepared using two photon polymerization. Off-center microneedles were created by changing the position of the channel relative to the central symmetry axis. The length of the microneedles would enable use for both delivery of pharmacologic agents and drawing of blood and/or interstitial fluids.

Keywords: ceramic, additive manufacturing, drug delivery

ABS 283

CERAMIC DENTAL IMPLANTS: HISTORY, STATUS, DEVELOPMENT IN PROGRESS

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(Yttria-stabilized Tetragonal Zirconia Polycrystal: Y-TZP) was introduced in dentistry and in orthopedics during the second half of the 1980s, thanks to its outstanding mechanical behavior due to tetragonal-monoclinic phase transformation. Studies carried out in-vitro and in-vivo, joined to clinical records evidence the excellent biological safety of this hi-tech ceramic.

In today dentistry, the uses of zirconia are manifold, the main ones being in dental implantology (fixtures and abutments), in restorative dentistry (CAD-CAM blanks as material for crowns, bridges, FPDs) and more recently in full contour zirconia crowns.

So far, a number of ceramic implant systems is on the market, enlarging the options available for dentists to best fulfill their patients' needs. The scientific literature shows that the osseointegration of zirconia and titanium implants is similar. In addition, ceramic implants are offering advantages over titanium in terms of aesthetics and hygienic properties. The concerns of a growing share of the public about sensitization to metals is also contributing to the increase the demand of metal-free devices in dentistry.

This presentation briefly reviews the evolution of ceramics dental implantology, the chemical-physical and mechanical properties of zirconia, the behavior of zirconia in the interaction with the implant environment. In addition, this presentation outlines the development now in progress in ceramic implantology based on new zirconia-based dispersion ceramics, the improvements introduced in the manufacturing processes, new design of implants and on the surface treatments aimed to improve the osseointegration of ceramic devices.

Keywords: dental implant, zirconia, ZTA

ABS 160

NATURE INSPIRES A NOVEL UNCONVENTIONAL APPROACH FOR 3-D BIOCERAMICS DEVELOPMENT

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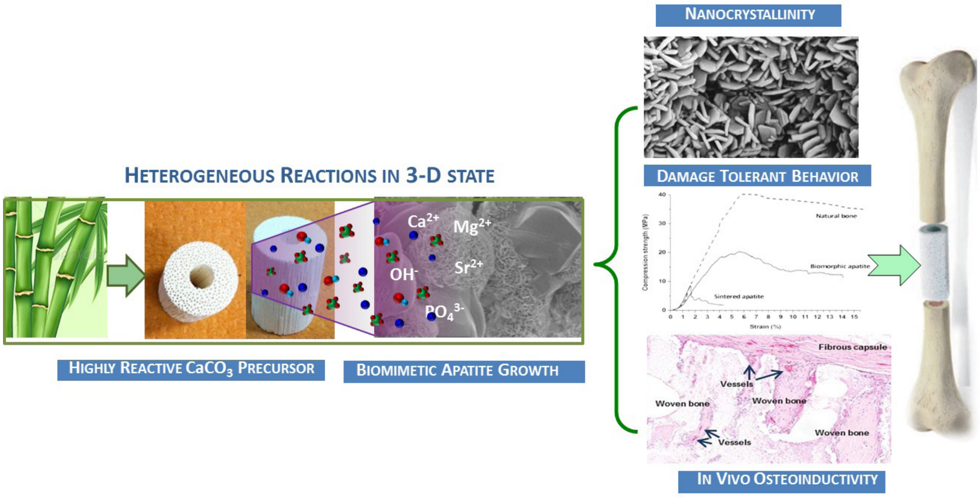
Substantial progress in bone regeneration is strictly related to developing 3-D biomaterials able to exchange chemico-physical and structural signals with cells and take part to metabolic processes to ensure the formation of mechanically-functional bone tissue. Calcium phosphates are widely reputed as elective materials for bone regeneration; however, the bone mineral is an inorganic phase characterized by multiple ionic substitutions and nanocrystallinity, at the basis of ability to exchange chemical signals with cells activating the biochemical osteogenic pathway. In this respect, the achievement of 3-D bioceramics retaining such bioactive chemistry and bone-mimicking multi-scale porosity has been so far prevented by the need of high temperature sintering treatments, which transform bone-like apatites into stoichiometric, stable and poorly bioactive phases.

The present work describes a new chemical approach for 3-D bioceramic development consisting in nucleation and growth of nanocrystalline, multi-doped apatite directly in the 3-D state, a process mediated by a wood template with bone-mimicking structure acting as a structural guide. Material processing at controlled temperature and gas pressure in supercritical conditions allows to control the kinetics of heterogeneous reactions occurring in the 3-D state, transforming the wood into calcium carbonate precursors characterized by high reactivity that permit subsequent transformation into nanocrystalline 3-D apatites by hydrothermal processes carried out at 200 °C. The process gives 3-D scaffolds with highly bioactive composition and multi-scale pore structure inherited by the original natural template. The scaffold shows nanostructure made of twinned apatite lamellae, organized into complex 3-D morphology showing high specific surface and multi-scale porosity opening to macroscopic channels typical of the original template, very relevant for vascularization and extensive bone penetration in the whole scaffold. The synergy between all these unique properties give the scaffold high strength and damage-tolerant mechanical behavior similar to natural bone. Furthermore, compressive and tensile tests show that the scaffold retain unique features typical of the original wood, confirming that inorganic bioactive devices with nature-inspired mechanical properties can be obtained by this new approach. Bioreactor tests report outstanding gene expression, if compared to a sintered macroporous hydroxyapatite scaffold. In vivo tests carried out with various animal models report osteoinductive ability in ectopic site and ability to regenerate long, load-bearing bone segments in sheep metatarsus with nearly complete resorption of the scaffold after six months. These results open to frontier applications in regenerative medicine, particularly in regeneration of long, load-bearing bone segments which is still an unmet need of very high impact.

Keywords: 3-D heterogeneous chemistry, Biomimetic hydroxyapatite, Damage-tolerant properties



ABS 128

BACKGROUNDS AND CLINICAL APPLICATION OF DENTAL CERAMIC IMPLANTS

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Titanium dental implants have provided a safe and evidence based standard care for the replacement of missing teeth for more than 50 years. But also ceramic dental implants have long since left behind their former rather marginal status as the exotics of implantology and are now increasingly being adopted in modern dental practice.
The health awareness of the general public and hence the increased demand for metal-free treatment options are also certainly factors in this perceptible trend.

However, the first available preclinical, as well as the short and medium term clinical data of the biomaterial zirconium dioxide show promising results and thus offer concrete practical advantages over titanium implants. These include healthier soft tissue, reduced peri-implant inflammation (peri-implantitis), no corrosion and improved aesthetics. Numerous clinical and preclinical studies have been able to prove these success factors of the new generation of ceramic dental implants.

In the past, ceramic dental implants were still subject to functional complications such as fractures and unacceptable failure rates. However, in recent years there has been a massive technological development in terms of material properties and design of the implant surfaces. Even in these aspects, modern implants made of zirconium dioxide already meet titanium implants at nearly the same level.

Today the developments are mostly dealing with the practicable and stable connection of the implant as the invisible part in the bone with the dental crown as visible part. Various concepts are currently available on the market: one-piece and two-piece implants, cemented, glued or screwed restorations. In two-piece ceramic implants the connection between fixture and abutment results challenging, due to materials properties. Titanium as metal is ductile, flexible and therefore connections are easier. On the other side zirconium dioxide as ceramic has no plasticity, is hard and sensitive to bending forces and therefore more difficult to connect. New approaches are being pursued with carbon fibre reinforced connecting bolts.

A further development of the biomechanical properties of the biomaterial ceramics and the development of long-term reliable connection concepts is desirable.
The prerequisites for this are basic knowledge of the clinical indications, the requirements of dental implant systems and the way of their application … as presented in this lecture.

Keywords: dental ceramic implants,clinical application,zirconium dioxide

ABS 55

CERAMICS AT THE NANOSCALE: IMPROVED BIOMATERIALS, DRUG DELIVERY VEHICLES, AND NOW IN SITU IMPLANTABLE SENSORS

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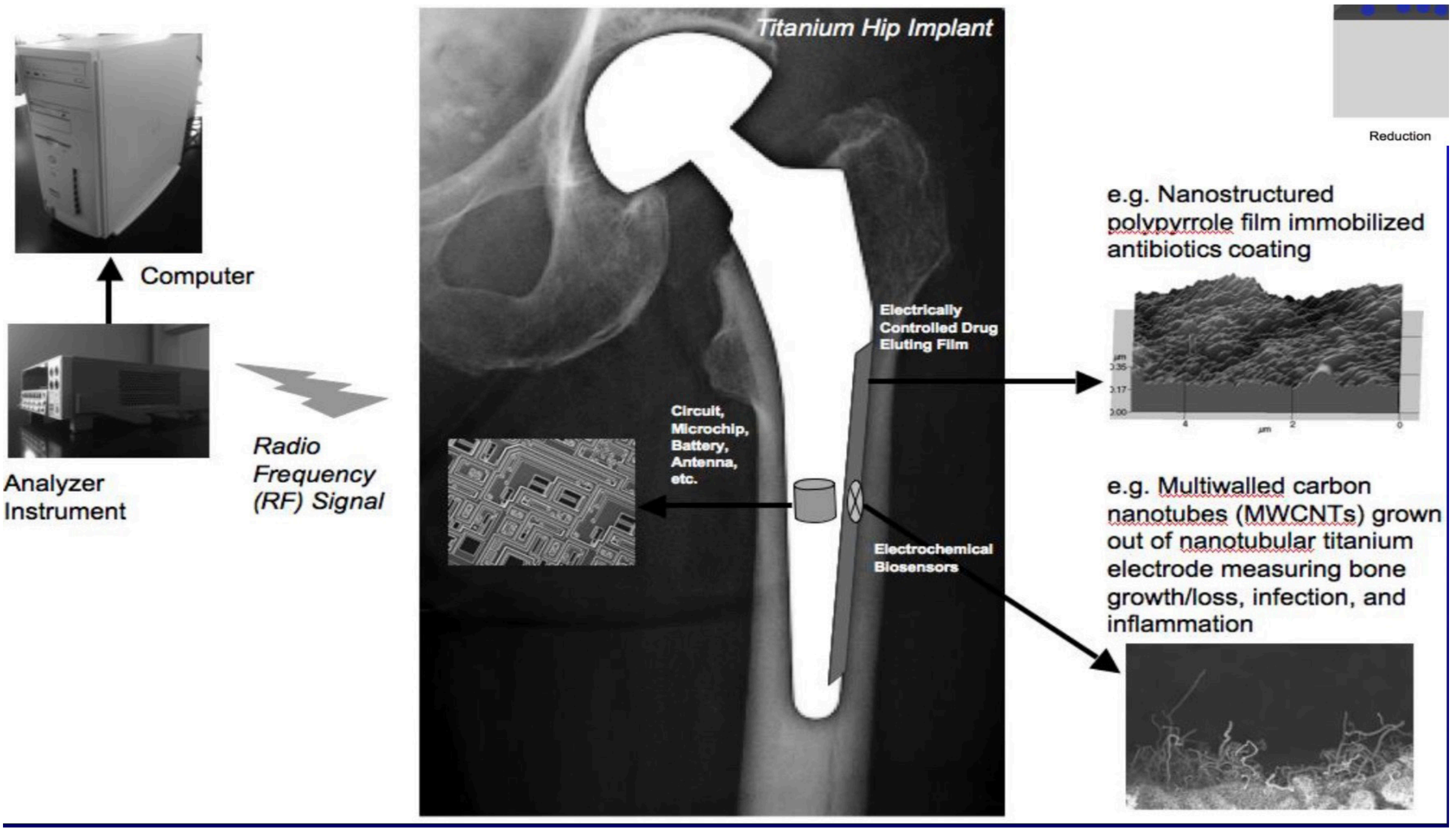
There is an acute shortage of organs due to disease, trauma, congenital defects, and most importantly, age related maladies. While tissue engineering (and nanotechnology) has made great strides towards improving tissue growth, infection control has been largely forgotten. Critically, as a consequence, the Centers for Disease Control have predicted more deaths from antibiotic-resistant bacteria than all cancers combined by 2050. Moreover, there has been a lack of translation to real commercial products. This talk will summarize how ceramic nanotechnology can be used to increase tissue growth and decrease implant infection without using antibiotics but using nano ceramic sensors (while getting regulatory approval). Our group has shown that creamic nanofeatures, nano-modifications, nanoparticles, and most importantly, nanosensors (Figure 1) can reduce bacterial growth without using antibiotics. This talk will summarize techniques and efforts to create nano ceramics including nanosensors for a wide range of medical and tissue engineering applications, particularly those that have received FDA approval and are currently being implanted in humans.

Figure 1 shows a nano ceramic sensor grown off of a hip implant which can detect in real time infection, bone growth, and inflammation. Moreover, it can send such information to an electronic device which can in turn control the release of nanoparticles to kill bacteria, inhibit inflammatory cells, and promote bone growth where and when needed.

Keywords: Implantable devices,Sensors,Drug delivery devices



S05

CERAMICS AND GLASSES FOR HEALTHCARE

ORAL PRESENTATIONS

ABS 857

Fe-DOPED CALCIUM PHOSPHATE NANOCOMPOSITES AS THERMO-SEEDS FOR THE HYPERTHERMIA TREATMENT OF CANCERS OF BONE AND BRAIN

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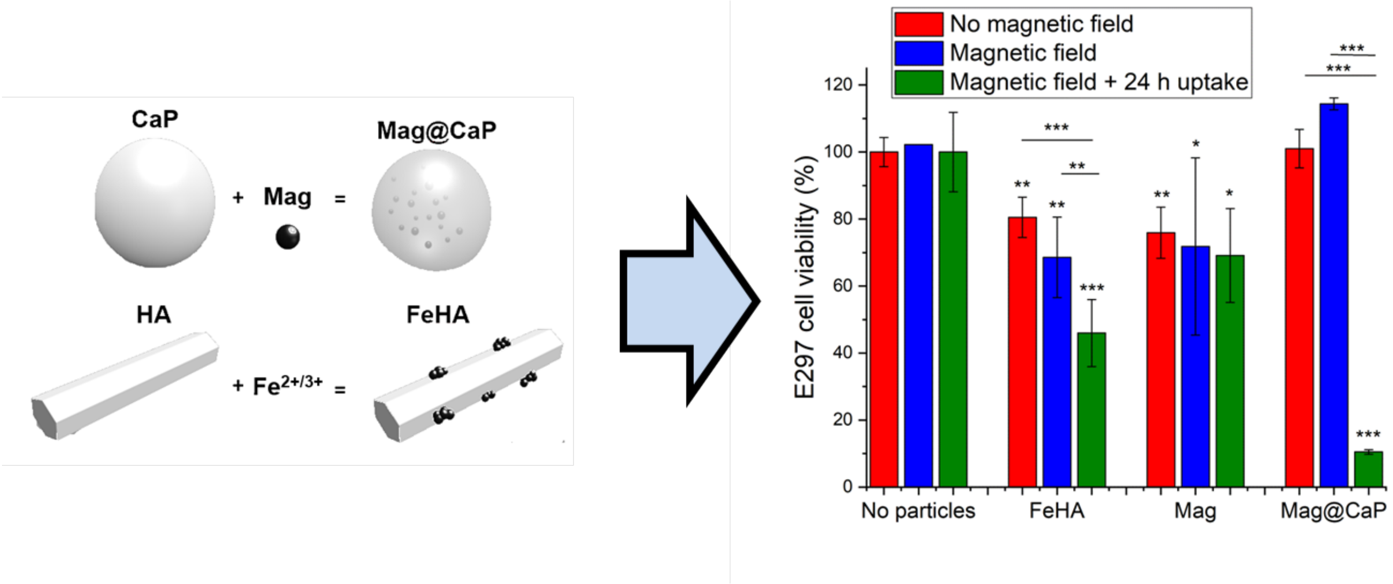
Magnetic hyperthermia is an cancer treatment modality with great potential in the therapy of glioblastoma and osteosarcoma based on the heating generation ability of magnetic nanoparticles under an alternate magnetic field. However, its applications are limited by the lack of selective susceptibility of neoplastic cells interspersed within healthy tissues. Here we describe the benefits of the use of two different types of magnetic calcium phosphates nancomoposites in the attempt to achieve this selectivity with respect to brain and bone cancers: iron-doped hydroxyapatite nanoparticles (FeHA) and iron oxide nanoparticles (Mag) coated with amorphous calcium phosphate (Mag@CaP). The most positive selectivity and targeting against cancer cells were exhibited by nonmagnetic amorphous calcium phosphate (CaP), as it increased the proliferation of human fibroblasts while it exerted toxicity on human glioblastoma cells (E297) at specific dosages. The addition of Fe to hydroxyapatite (HA) consistently benefitted healthy cells, while synergistic effects, positive for glioblastoma and negative for osteosarcoma, were observed upon combining Mag and CaP. The uptake up tp 24 hours of the tested nanocomposites was a prerequisite for the reduction of cancer viability in alternate magnetic fields of extremely low power, and sheer adsorption onto the cell membrane was not sufficient to produce the same effect. This effect was extremely significant for Mag@CaP or FeHA and negligible for Mag, demonstrating definite benefits of combining magnetic iron with calcium phosphates. Such selective effects are important in the global effort to rejuvenate the clinical prospects of magnetic hyperthermia.

Keywords: Magnetic calcium phosphate, Composite nanoparticles, Magnetic hyperthermia



ABS 856

MICROSTRUCTURAL AND BIOLOGICAL CHARACTERIZATION OF HYBRID PLA/BIOGLASS 45S5 COMPOSITE SCAFFOLDS FOR BONE REPAIR

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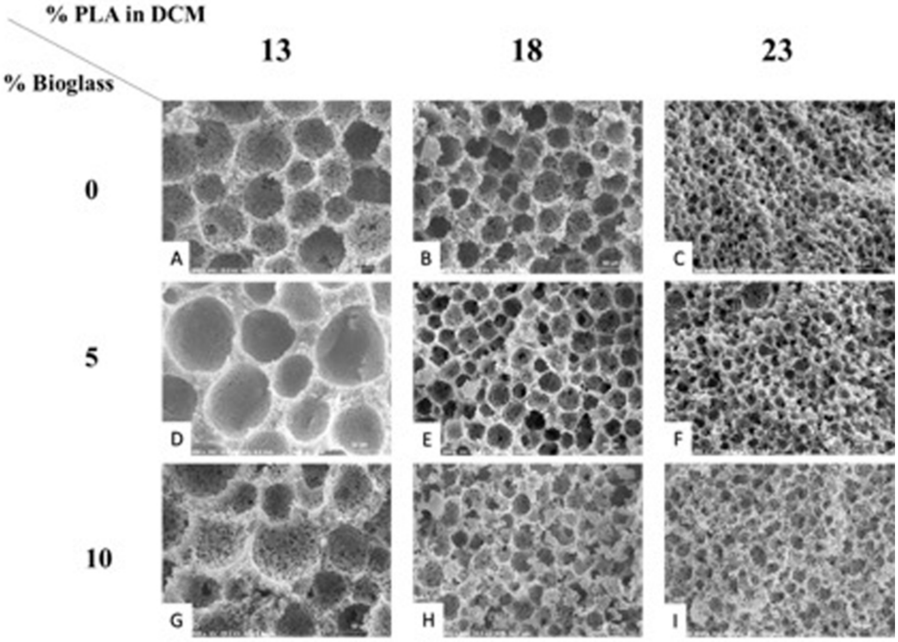
Three-dimensional, interconnected porous scaffolds composed of polylactic acid (PLA) and bioglass 45S5 were fabricate by the nonsolvent thermally-induced phase separation technique (NTIPS) in the PLA-Dichloromethane (DCM)-Hexane system at -20°C; 5, 10 and 15 wt.% of bioglass 45S5 powder amounts were added as reinforcement. The bioglass 45S5 powder was prepared by the melt-quenching technique with an average particle size of 14 μm and surface area of 0.42 m2/g. The porosity of the scaffolds was evaluated by scanning electron microscopy and X-ray microtomography obtaining pore sizes ranging from 1 to 250 μm and average porosity of 50%; the morphology of the scaffolds was modified as the amount of PLA and bioglass 45S5 increased, obtaining lower porosities and rougher surfaces. The hybrid composite scaffolds were semi-crystalline with 55 to 67% crystallinity, the crystallinity being an important parameter in the degradation rate of the material; the contact angle of the material was evaluated with two different liquids: water and formamide, determining the surface energy of the scaffolds by the mathematical arrangement of Owens-Wendt-Kaeble; scaffolds had a hydrophobic behavior with contact angle values above 120°, and low surface energies with the exception of the 13PLA/5BG scaffold.

Keywords: Bioglass, PLA, NTIPS



ABS 854

HIGH STRENGTH AND TRANSLUCENT NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA FOR DENTAL APPLICATIONS: PROCESSING AND CHARACTERIZATION

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3 mol. % Yttria-stabilized Tetragonal Zirconia Polycrystal (3Y-TZP) is one the well known engineering bioceramics due to its exceptional strength (>1000 MPa), transformation toughening behavior (KIc of 5-10 MPa.m0.5), wear resistance, and biocompatibility. These properties, associated to its white color and reliable shaping processes by computer aided design/computer aided manufacturing (CAD/CAM) have made 3Y-TZP attractive dental restorative material for multi-unit or single tooth restorations. Nevertheless, the limited translucency of standard 3Y-TZP is a major drawback for fabrication of aesthetic monolithic dental pieces. A recent trend is to improve translucency by increasing the yttria content (>4 mol. %) while limiting the pore size and volume fraction (e.g., to <200 nm and 0.05%, respectively). However, these commercial highly translucent materials represent only a compromise due to their lower mechanical performance. An alternative strategy is to reduce light scattering by decreasing the final grain size, e.g. to <150 nm. Such structure can be obtained after conventional sintering by using highly reactive nanoparticles as starting material. In this case, the initial particle size, the choice of shaping method, the density of green bodies, and the sintering protocol play a crucial role for successfully improving the optical properties of the final product. To practically achieve the nanocrystalline structures with minimum porosity and defects, the challenges of i) processing homogeneous, high-density, and crack-free green bodies at clinically relevant thicknesses from fine nanoparticles and ii) densification into nano-grained samples with optimized microstructure have to be addressed.

In this study, we report the fabrication of 3Y-TZP green bodies from nanoparticles with primary size of <10 nm that can be fully densified to translucent samples with a final grain size of <100 nm using conventional radiant dental furnaces. We studied the effect of grain size on mechanical (biaxial strength and indentation fracture toughness) and optical properties (real in-line and total forward transmission, translucency and opalescence factor) and compared them with those of commercially available standard 3Y-TZP and high translucency zirconia. It was observed that by decreasing the grain size, the light transmission of the samples can be significantly improved up to 50% of incident light. In addition, thanks to good homogeneity and very small critical defect size, samples with a grain size of even <100 nm can still display biaxial strength competing with standard, sub-micron grain size 3Y-TZP.

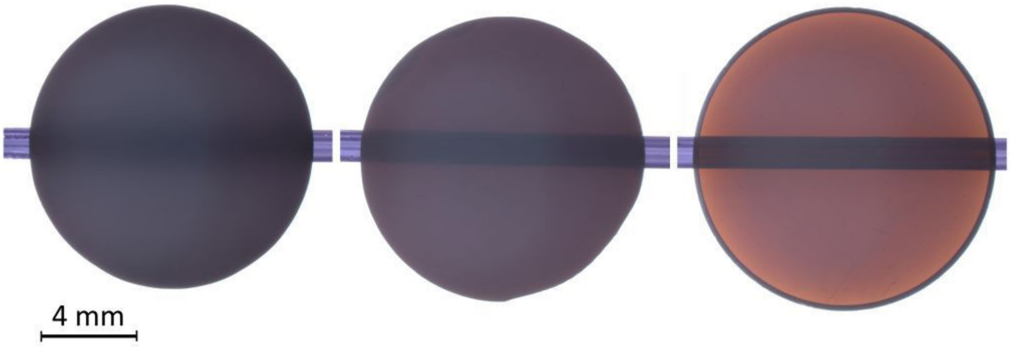

Figure 1. Appearance of 1 mm-thick samples after polishing under transmitted light; left) standard 3Y-TZP, middle) high translucency zirconia, and right) nano-grained 3Y-TZP reported in this work. Images were captured under same illumination and capture and background conditions.

Keywords: Tetragonal Zirconia, Translucency, Dental restorations

ABS 839

ROBOCASTING OF HYDROXYAPATITE-BASED SCAFFOLDS WITH MULTI-SCALE POROSITY

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Objective Scaffolds for bone tissue engineering must possess several characteristics in terms of cellular activity and porosity [1]. Given that hydroxyapatite is a calcium phosphate whose chemical composition is similar to the chemical composition of the mineral bone [2], it is employed as the main material. The size of the interconnected macropores of the elaborated parts is fixed between 300 µm and 400 µm in order to promote bone-tissue in-growth. The fabrication of three-dimensional periodic scaffolds with such architecture is enabled by robocasting, an additive manufacturing process based on the micro-extrusion of a viscous paste through a nozzle. This elaboration implies the formulation of a high-solid-content paste in order to achieve the right rheology for robocasting, to prevent cracking during drying and to maximize the density of the scaffolds after sintering. The sintering parameters also have to be adjusted to monitor the microporosity volume fraction.

Materials & Methods The hydroxyapatite is synthetized through an aqueous precipitation method [3]. Afterwards, the paste is prepared by mixing: the calcined and milled hydroxyapatite powder with a dispersant, a plasticizer/lubricant and a binder, which consists of a gel containing deionised water and a jellifying agent. Then, the paste is deposited through a nozzle (diameter equal to 400 µm) by robocasting so as to create macroporous scaffolds of 1×1×1 cm with a center-to-center distance between the rods of 400 µm. The dried green parts are sintered with determined thermal cycles to control degrees of densification and therefore microporosity volume fractions. The sintered parts are observed by Scanning Electron Microscopy and their density is determined by Archimedes' method.

Results Three-dimensional porous scaffolds have been built by robocasting with a paste containing 47 vol% of hydroxyapatite (Fig. 1). Furthermore, the macropore size of the sintered networks, between 300 µm and 400 µm, corresponds to the dimensions necessary to bone-tissue in-growth. The sintering temperature and the dwell time enable to obtain various degrees of densification and thus various microporosity volume fractions.

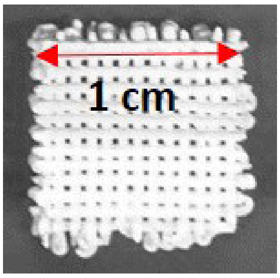

Fig. 1. Photograph of a hydroxyapatite scaffold produced by robocasting

Conclusions This work demonstrates that robocasting allows for the fabrication of multi-scale porosity hydroxyapatite-based scaffolds.

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Keywords: hydroxyapatite, ceramic scaffolds, robocasting

ABS 830

ADVANCED SOLID STATE NUCLEAR MAGNETIC RESONANCE EXPERIMENTS FOR THE CHARACTERIZATION OF SUBSTITUTED HYDROXYAPATITES

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Apatites are a class of complex and diverse materials that have gained importance because of their biological role. One of the major constituents of bone and hard tissues in mammals is a calcium phosphate whose structure closely resembles hydroxyapatite, Ca10(PO4)6(OH)2. This biological apatite is poorly crystallized, non-stoichiometric with multiple cationic and anionic substitutions.

Hydroxyapatite is also found in pathological calcifications. Indeed, the first steps for the formation of some kidney stones may involve deposits of nanocrystalline carbonated hydroxyapatite, commonly called Randall plaques, which are considered nucleation centers. Apatite growth can also be promoted by bioactive synthetic materials used as implants and these biomaterials play a major role in the manufacture of artificial bone material and as a coating on surgical implants.

In all these examples, the apatite phase is nanocrystalline or amorphous with a chemical composition that varies due to the ability of the structure to accommodate a large number of cationic or anionic substituents. This structural versatility allows precise adjustment of the properties in terms of bioactivity, but makes difficult the characterization of these substituted apatites.

This presentation will highlight how the use of multidimensional solid-state NMR techniques recently coupled with Dynamic Nuclear Polarization (DNP) allows for better structural characterization of synthetic or biological substituted apatites. NMR/DNP allows an unprecedented description of carbonate substituted hydroxyapatites. Key structural questions related to order/disorder and clustering of carbonates are tackled using distance sensitive DNP experiments. Although 43Ca should be a fundamental NMR target in the field of biomaterials, it suffers from an intrinsic low sensitivity. Nevertheless, 1H - 43Ca 2D experiments were recorded at natural isotopic abundance in short experimental time, and for a restricted mass of sample, opening avenues for the detailed atomic-scale description of interfaces in biological apatites, which is of primary importance to understand their structure and properties.

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Keywords: Nuclear Magnetic Resonance, Substituted Apatites

ABS 117

COPPER DOPED-HYDROXYAPATITE: FROM POWDER SYNTHESIS TO BIOCOMPATIBLE CERAMICS

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Synthetic scaffolds made of calcium phosphate hydroxyapatite (HA) are widely used to repair damaged bone tissues. Scaffold vascularization is an essential factor for new bone formation and ingrowth within the implant porous network. Some studies showed that copper improves angiogenesis [1], therefore this project focuses on the processing of copper-doped HA ceramics and on the evaluation of their biocompatibility in vitro.

The synthesis of copper-doped HA powders was first performed by co-precipitation: a phosphate solution was added to an aqueous solution of calcium and copper precursors and matured five hours at 80°C and pH 8. Solid state reaction was also envisaged. In this case, pure HA powder, synthetized by precipitation, was mixed with several rates of copper oxide powder and milled in an aqueous medium. The thermal behavior of the powders was investigated. For powders precipitated with a reactant molar ratio (Ca+Cu)/P = 10/6, a secondary phase of tricalcium phosphate always appears above 800°C. With a ratio Ca/P = 10/6, a biphasic mixture of apatite and CuO is obtained that transforms in a single phased apatite after heating at 1050°C. The same result is obtained using the direct solid state reaction by heating HA and CuO powder mixtures which appears to be the easier route to synthetize phase pure copper-doped HA.

The copper insertion in the apatite crystal lattice at the 2b (0,0,0) Wyckoff position is confirmed by Le Bail and Rietveld analyses. The color change from grey to purple during heating suggests a mixed-valence compound Ca10(PO4)6(OH)2-2x-yCu2+xCu+yO2x+y. This chemical composition is in agreement with recent works [2]. Cu-doped HA ceramics containing up to 5 wt% were directly processed by reaction sintering of HA and CuO powder mixtures from 1050 to 1200°C. Samples with a densification rate above 95 % are obtained. The addition of copper induces a small shift of HA sintering temperature of 20°C towards higher temperatures. From 1100°C substantial grain growth is observed whatever the doping rate. The phase purity and homogeneity of copper distribution were checked using XRD and STEM. Biocompatibility assays are under progress in order to determine the cell-friendly copper rates and the results will be presented too.

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Keywords: Hydroxyapatite, Copper, Biocompatibility

ABS 798

DEVELOPMENT OF POLYMER DERIVED Sioc CERAMICS AS AN IMPLANT BIOMATERIAL

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Polymer derived silicon oxycarbide ceramics (PDC-SiOC) are interesting candidates for fabrication of micro-sized ceramics with the highest precision. Development of strategies for micro-manufacturing of high precision ceramic components based on PDCs, for biomedical applications, serves as the main focus of our research programme. Our approach also includes functionalization of the liquid polymer precursors with nanomaterial fillers, for instance carbon-based, so that new and improved properties (electrical, mechanical, biological) can be conveyed to the final ceramic product. PDC synthesis starts with cross-linking liquid polymer precursors followed by pyrolysis at temperatures above 800 °C to obtain final ceramics. Cross-linking of preceramic precursors serves as an important part of the process to fabricate preceramic green bodies. A platinum catalyzed hydrosilylation method is used in our approach for crosslinking the starting precursors. Stereolithographic methods such as 2 photon polymerization have also been successfully employed for the fabrication of micro-sized preceramic green bodies. Pyrolysis at high-temperature and controlled atmosphere then convert the green- into the ceramic micro-product. The polymer to ceramic conversion happens mainly at a temperature between 400 - 1000 °C with redistribution of C and O atoms around silicon. Microstructural properties of the ceramics are found to be significantly influenced by phase separation during sintering at temperatures above 1200 °C leading to crystallization of SiC and SiO2. Enhancement in the electrical conductivities along with degradation in flexural strength is observed after pyrolysis at 1400 °C. Investigations of these materials for blood contact applications revealed higher levels of blood coagulation on top of 1400 °C ceramics in comparison with 1000 °C ceramics. Good cell adhesion with no cytotoxicity is observed during cell culture on the surface of 1000 °C ceramics. Properties of these materials can be further improved by dispersing nanofillers (e.g. CNTs, TiO2 etc.) in the starting polymer precursors. More detailed investigations including in situ measurement of ceramic sintering and biocompatibility under pacing conditions are also in progress and they are expected to provide valuable information on the kinetics of the phase separation and the dispersion of nanofillers in the final ceramics, including its influence on microstructure evolution.

Keywords: Bioceramics, Polymer derived ceramics, Biomedical implants

ABS 760

POLYMERIC CERAMIC COMPOSITES FOR THE TREATMENT OF RHEUMATOID ARTHRITIS

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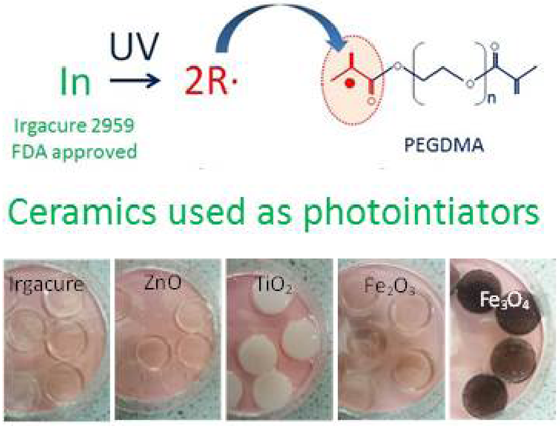
Rheumatoid Arthritis (RA) is an autoimmune disease of unknown etymology which is characterized by chronic inflammation of the joints and surrounded tissue. It entails the progressive destruction of joints and irreversible sequels that in the 10% of the cases involve permanent disability. [1-3] Current treatments are basically palliative treatments which prevent the joints degradation, relieve the pain and maintain the articular force and function. [4] Many studies relate the RA with high levels of free radicals. [3]They have been even related with the chronicity as well as the destructive consequences of the illness.

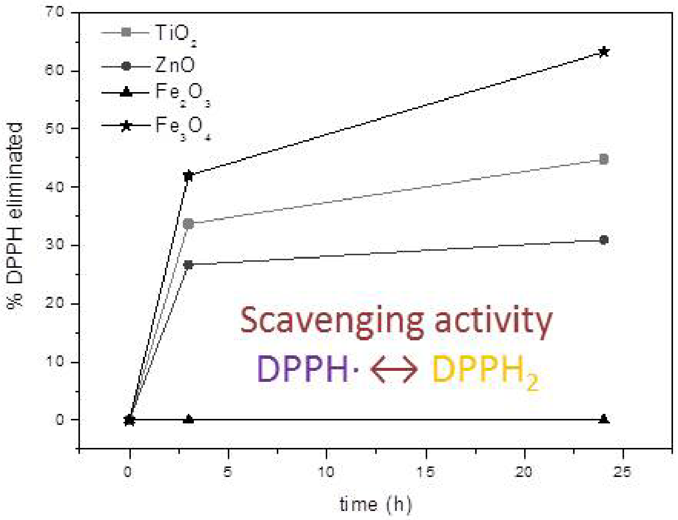
In the present work, polymeric-ceramic composites are developed for the fabrication of implantable devices able to neutralize free radicals to avoid the inflammatory process and the progress of the disease.

These materials are composed by micrometric powders of ZnO, Fe2O3 or Fe3O4 which are embedded in a polymeric matrix of polyethylene dimethyl methacrylate (PEGDMA). Ceramic powders play two main roles: first, in monomer solution and presence of UVA light, they will photoinitiate the polymerization process to obtain to fabricate the composites; and second, once the composite are implanted, and in absence of light, they will neutralize the radical species. [5-7] The capability to neutralize radical species is known as scavenging activity. This property has been already studied in some semiconductive ceramic materials such us some titanium oxides. [8] The size of ceramic particles play an important role. Whle micrometric particles neutralize radical species in absence of light, nanometric particles promote the production of radicals despite of the dark conditions. [9] Moreover, the use of micrometric particles avoids nanotoxicity complications. The polymeric matrix regulates the arrival of the free radicals existing in the physiological fluids to the surface of the ceramic powders due to the swelling behavior of hydrogels.

The capability to neutralize free radicals by the ceramic powders as well as their capability to photoinitiate the polymerization process will be studied. Both activities will be studied for all the ceramics prosed and compared between then. Moreover, the gel fraction and swelling behavior will be measured. Gel fractions higher than 60% have been obtained using micrometric powders of ZnO, Fe2O3 or Fe3O4 as photoinitiators and Fe3O4 shown the best scavenging activity.

Keywords: Photopolymerization, Rheumatoid Arthritis, Scavenging Activity





ABS 758

A NEW BIOGLASS WITH ULTRA-HIGH CRYSTALLIZATION TEMPERATURE AND OUTSTANDING BIOLOGICAL PERFORMANCE

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In the last decades, the need for repair and regeneration of bone and tissues has dramatically emerged, because of the world population ageing. As a matter of fact, millions of people every year need a surgical procedure intended to replace missing or lost bone.

Among other bioceramics, bioactive glasses have proven to be effective in forming a strong bond with bone tissue in vivo and thus have been extensively used in orthopaedics and dentistry.

Moreover, some specific compositions, including the gold standard bioglass 45S5, can bind both to hard and soft tissues, may have an antibacterial effect, and stimulate angiogenesis and neovascularization.

Despite these interesting properties, bioactive glasses have shown some drawbacks, i.e. the tendency to crystallize during thermal treatments, which are necessary in several processing routes. In fact, crystallization inhibits or al least decreases the bioactivity.

Therefore, some attempts have been made to modify the composition in order to obtain glasses with higher crystallization temperature.

In this work, a novel bioglass, characterized by a newly designed composition, is presented. This bioglass, called BGMS10, contains strontium and magnesium and has a low content of alkali oxides. BGMS10 is characterized by a remarkably higher crystallization temperature (932°C) than 45S5, a larger processing window and it can be sintered at lower temperature (737°C). Thus it can maintain its amorphous nature upon processing and consequently a pronounced bioactivity. For these reasons, this novel bioglass can be considered a great candidate for the realization of specific products which require a thermal treatment, such as scaffolds, composites and bioactive coatings.

Moreover, in vitro tests confirmed the biocompatibility and the absence of cytotoxicity of such material, as recommended by standard procedure (ISO 10993).

Furthermore, bioactivity of the material was evaluated by using an innovative 3D cellular model, applied for the first time to a bioglass. In fact, osteoinductivity of the biomaterial was studied with a cellular model that mimicked the potential clinical application of BGMS10 in in the orthopaedic field: human bone marrow mesenchymal stem cells (BM-MSCs) were utilized in this 3D cellular model.

Keywords: Bioactive glass; Magnesium oxide; Strontium oxide; Sintering; Thermal properties; High crystallization temperature; Mesenchymal stem cells; bone regeneration, cell culture, bioactivity

ABS 746

INNOVATIVE SYNTHESIS AND CONSOLIDATION OF HYDROXYAPATITE FROM BIOGENIC CALCIUM CARBONATE SOURCES

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Recent works have shown that hydroxyapatite bioceramics synthesized from calcium-containing natural sources is more similar to the biological one and shows better bioactivity.

Calcium orthophosphates have a special importance for bone tissue engineering because they represent the inorganic part of the natural bone. Among these, hydroxyapatite (HA) Ca10(PO4)6(OH)2 and β-tricalcium phosphate β-Ca3(PO4)2, are the most widely studied due to their excellent biocompatibility and osteoconductive properties. However, synthetic HA differs from the mineral phase of natural bone because this is a non-stoichiometric calcium-deficient compound that includes also ions and trace elements that play a significant role in the development of bone. Usually, HA obtained of biological origin results more similar to natural bone and is therefore more bioactive.

In this work, biogenic calcium carbonate precursors from cuttlefish bones, chicken eggshells and mussel shells were used to synthesize hydroxyapatite via mechanochemical method in ammonium phosphate solution with the aim to retain most of the organic part of the raw material which might be beneficial for osteoconductivity. The synthesis method allowed also to produce nanosized materials in very short time. Chemical composition, microstructure and morphology of the produced nanopowder were analyzed in terms of processing conditions like pH, temperature and solid content of the slurry.

Some of the synthesized calcium-phosphates were also consolidated by cold sintering and field-assisted methods to maintain the very fine nanostructure also in the final product.

Keywords: Biogenic calcium carbonate, Flash sintering, Mechanochemistry

ABS 664

DIGITAL LIGHT PROCESSING OF BIOACTIVE GLASS-CERAMIC COMPLEX STRUCTURES FOR BONE TISSUE REGENERATION

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We present the Digital Light Processing (DLP) fabrication of different glass-ceramics in complex structures starting from homogenously dispersed glass particles in a photosensitive polymer matrix. Highly complex Bioactive glass-ceramic structures were fabricated by additive manufacturing using stereolithography of photocurable polymers filled with bioactive glass particles. Bioactive glass-ceramics, with different and complex geometries, formed after heat-treatment in air. Besides the uniform and homogenous shrinkage, the control of viscous flow during firing was achieved resulting in a complete shape maintenance after sintering. Complex structures with porosity up to 85 vol% possessed mechanical properties of ~ 4MPa, were successfully fabricated. The bioactivity of the developed glass-ceramics together with the design freedom and high resolution of 3D stereolithography printing make these glass-ceramic structures suitable candidates for bone tissue engineering.

Keywords: Additive Manufacturing, Stereolithography, Bioactive glass-ceramic

ABS 650

A NOVEL TECHNIQUE BASED ON FUSED DEPOSITION MODELLING TO OBTAIN 3D FULL-CERAMIC SCAFFOLDS

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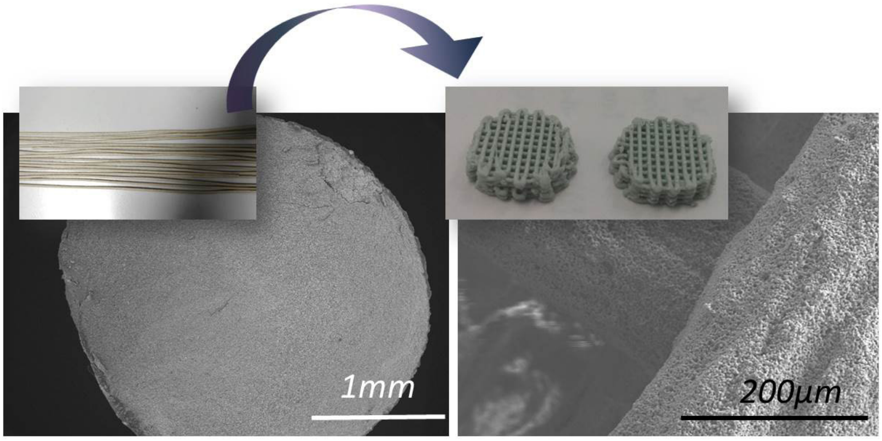
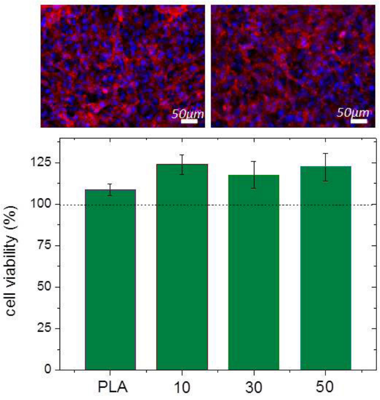
The additive manufacturing (AM) techniques are arising as the most appropriated techniques to produce customized 3D pieces with complex structures and geometries. This group of techniques has been applied in different industries but biomedicine has gained a special attention because patient-customized products are often required. Well-known AM techniques for processing of ceramics inks are binder jetting, inkjet technology, stereolithography (SLA) and robocasting. All of these methods allow printing of green samples with complex structures with a good control on composition and microstructure, like scaffolds for biomedical application. Among AM techniques, the fused deposition modelling (FDM) is one of the most simple and inexpensive techniques, which allows high printing speeds using thermoplastics as structurers.
On the other hand, hydroxyapatite (HA) is a bioceramic similar in composition to the mineral component of human bones. Several review its exceptional properties such as no toxicity, biocompatibility, bioactivity, osteoconductivity and good osteointegration properties. This work is aimed to produce available HA modified granules feedstock to process full inorganic scaffolds by FDM, following a patented procedure (nº: 201830503). The thermoplastic behavior of the HA feedstock as well as the particles packing and dispersion depend on the processing additives used and mixed with HA particles through colloidal processing. The stability and dispersion of the ceramic particles is provided by their surface modification with polyelectrolytes or surfactants which also allow enhancing the interfacial interaction between HA and thermoplastic additives. This dispersion is studied by rheology as a function of the thermoplastics agent selected, PLA (Poly-L-lactic acid or Poly-L, D-lactic acid) and PEG (Polyethylenglicol). Both are thermoplastic polymers with exceptional biocompatible properties. Regarding to the hybrid feedstock homogeneity, it is possible to increase the ceramic load as high as 78wt.% without compromising the thermal stability of the polymer. Ceramic particles/Polymers composition and developed links during the thermal-shaping are studied in terms of zeta potential, ATR-FTIR, and DSC. This processing procedure leads to ceramic porous scaffolds suitable for the biomedical industry without modifying their biocompatibility.

Keywords: Fused deposition modelling, Hydroxyapatite scaffolds, Particle surface modification





ABS 645

HYBRID INJECTABLE PLATFORMS FOR THE IN SITU DELIVERY OF THERAPEUTIC IONS AND DRUGS FOR BONE REGENERATION

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In the field of bioceramics, mesoporous bioactive glasses (MBGs) have received significant interest in the past decade as powerful systems to support bone regeneration. However, in the presence of compromised remodelling process (e.g. delayed bone healing, osteoporosis, bacterial infections), the effective treatment of bone fractures still represents a challenging clinical issue.

More recently, with the aim to face this clinical need through highly targeted therapies, a new class of versatile and multifunctional nanobiomaterials based on MBGs containing specific therapeutic elements has been explored. In particular, MBG composition has been enriched with controlled amount of selected ions, as Sr2+and Cu2+, whose release is able to impart specific biological functions, including anti-bacterial activity, as well as stimulation of osteogenesis and angiogenesis [1]. In addition, due to their well-defined and accessible porous structure, MBGs can store and release drug molecules (i.e. anti-oxidants, antibiotics) and their surface functionalization can impart specific properties to these nanocarriers (i.e. sustained drug release, targeting properties).

In order to concentrate and maintain the multifunctional carriers at the pathological site and to guarantee in situ and prolonged release of ions/drugs, the conjugation of these nanocarriers with a vehicle phase based on thermosensitive hydrogels [2] represents an effective strategy.

In this contribution, MBGs containing therapeutic ions (i.e. Sr2+, Cu2+) in the form of micro- and nanoparticles have been loaded with different drugs (i.e. ibuprofen, N-acetyl cysteine). Loaded MBGs were characterized through FESEM/EDS, N2 adsorption-desorption, DLS, zeta potential measurements, TGA/DSC analysis and in term of ion and drug release properties. MBG nanocarriers were embedded into a polyurethane-based hydrogel to develop an injectable thermosensitive formulation, able to undergo a complete sol-gel transition in physiological conditions [3]. The resulting hybrid formulations were characterised in terms of sol-to-gel transition temperature and time, injectability and stability in aqueous environment at 37 °C.

MBG-containing hydrogels showed fast gelation and injectability in a wide range of temperatures through different needles. The release profiles of ions and drugs from embedded MBGs were assessed, evidencing the ability to remain in situ for several days, thus allowing the release of therapeutic ions and drugs with a sustained and prolonged kinetics with respect to MBG particles as such.

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Acknowledgments
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Keywords: bioactive glasses, therapeutic delivery, thermosensitive hydrogel

ABS 628

STABILISED ZIRCONIA/CALCIUM PHOSPHATE COMPOSITES FOR BONE IMPLANTS

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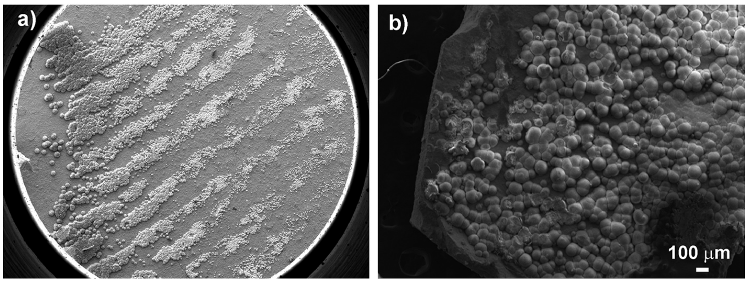
Stabilized zirconia ceramic with good mechanical properties, is widely applied for orthopedic and dental restoration. Zirconia is a biocompatible but bio-inert ceramic material, meaning it poorly or not at all interacts with the surrounding tissue and cannot connect with hard tissues. Stabilizing compounds such as yttria, magnesia, ceria, and alumina are commonly used to stabilize the metastable tetragonal phase in a zirconia, thus enabling transformation toughening. On the other hand, calcium phosphate (CaP) based biomaterials are often used as coatings for bio-inert metal and polymer implant materials. With the aim to prepare bioactive materials for bone implants, we investigated growth and stability of CaP coating on porous ZrO2 obtained by sol-gel process. In order to test their suitability as a material for possible bone implants mechanical properties of these composite bioactive ceramics was tested by ball to ball compression test, indentation hardness test and by scratch test. The aim of this work was to prepare porous stabilized zirconia ceramics and to study potential of use CaP as its bioactive coating. Capability of porous zirconia ceramic to induce formation of calcium phosphate in metastable solution was studied. Biomimetic process of applying calcium phosphate (CaP) on the surface of porous ZrO2 ceramics was used. This procedure is based on the deposition of calcium phosphate from solution under conditions close to those in the that is at physiological temperature, pressure and pH. Yttria-stabilised zirconia with 10 wt% yttria was prepared by sol-gel process. Obtained powder was uniaxially pressed and sintered in air for 8 h at 1000, 1200 and 1400 °C with the aim to form ceramics of different porosity. The ability of ZrO2 ceramics to induce calcium phosphate growth was tested by immersing the plates into the metastable calcifying solution. The structure and morphology of zirconia ceramics and CaP growth were studied by scanning electron microscopy, Raman spectroscopy and X-ray diffraction. In order to test their suitability as a material for possible bone implants, mechanical properties (strength, hardness and density) of the ceramic with and without coating were measured. We observed that prepared zirconia ceramics were able to initiate formation of calcium phosphates from metastable solution. The growth of CaP coatings and its morphology will be discussed taking into account ceramics porosity. It was shown that obtained CaP was calcium deficient hydroxyapatite (CaDHA), but the cowering of the zirconia ceramic surface by CaP, were dependent on the procedure of washing ceramic surface before immersion of ceramics in calcifying solution (Fig 1). It was shown that CaP coating did not influence mechanical properties. The mechanical characteristics of porous zirconia will be discussed and compared with known properties of the bones.
Fig. 1: CaP growth during 14 days on ceramic washed by: a) H2O and etahanol, b) HCl, H2O and Ethanol

Keywords: Stabilized zirconia ceramic, calcium phosphate, mechanical properties



ABS 624

STRUCTURE AND PROPERTIES STUDY ON STRONTIUM AND FLUORINE-SUBSTITUTED HYDROXYAPATITE

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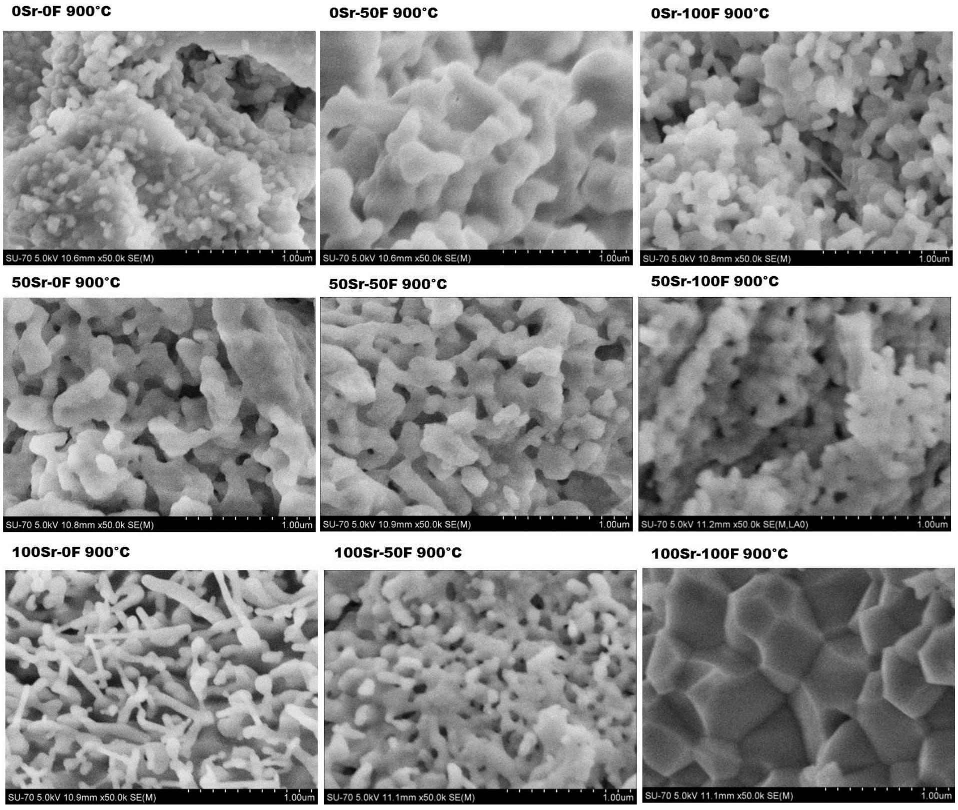
Objective The aim of the project is to synthesize a series Sr, and F substituted apatite with different heat treatment temperatures. The role of the chemical compositions on crystal structure, the relationship between various chemical modifications and their morphology properties is established. The results of this project will help to understand how the different anions and cations substitutions modify the apatite lattice, and what the role of the heat treatment temperature has on apatite structure modification. This study would be beneficial for the design of innovative biomaterials, in implantable medical devices fabrication, coating and drug delivery applications

Materials and Methods Substituted hydroxyapatites were prepared by solution method based on G.Penal' method. The precipitated apatites have been heat-treated at 300, 600 and 900°C for 2 hours. All the samples are characterised by ssNMR, XRD and SEM.

Results The co-relationship between different ion substitutions and crystal lattice parameters have been established, Further SEM study reveals the role of the chemical compositions on the apatite morphology (Figure 1).

Conclusions: The conclusion shows the different ion and cation substitutions has a strong impact on the crystal shape and size. In FHA structure, the relative small F ions are in the middle of the Ca triangles. F ions substitution has more influence on the a axis than the c axis. It suggests that the ion substitution is random along the c channel and form the solid-solution at the beginning. However, the solid solution structure is sensitive to the heat treatment temperature. When the heating temperature higher than 600°C, the F ions shows the tendency of separation from the F-OH mixture and segregated to form F rich region. Comparing with the F ions substitution, strontium substitution alters the lattice size significantly. Both a and c axis enlarge with incorporating the larger cations, and with increasing the Sr substitutions, the a/c reducing, which suggests the crystal grow along the c axis. Moreover, the Sr-Ap shows little influence on the elevating heat treatment temperatures. Further SEM study suggests that the grain size reduces steadily with increasing Sr content in apatite. Sr substitution facilitates the apatite nucleation and forms the larger crystallites. Meanwhile, fluoride substitution also forms the dense lattice due to the reduction in the volume of the unit cell. The dense morphological feature of 100Sr-100F could also improve the mechanical strength of the apatite materials significantly.

Keywords: Hydroxyapatite, Strontium hydroxyapatite, XRD, NMR, SEM



ABS 581

IMPACT OF THE CARBONATION REACTION ON THE HYDROXYAPATITE SINTERABILITY

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Carbonated hydroxyapatite (CHA) represents a real potential for bone tissue engineering thanks to their increased solubility and biodegradation rate, which can be controlled via the quantity of substituted carbonate. Carbonate ions can be incorporated at two different sites in the hydroxyapatite (HA – Ca10(PO4)6(OH)2) lattice, either at the phosphate site (B-site) through chemical synthesis by aqueous precipitation, or at the hydroxide ion site (A-site) through thermal treatment under gaseous carbon dioxide (CO2). To stabilize B-type CHA up to a temperature enabling their sintering, a CO2 gas partial pressure is necessary. It induces a carbonation of the A-sites through the following reaction CO2(g) + 2 OHOH = CO3-OH + V+OH + H2O(g) (1), which could change in turn the sinterability. Indeed, previous work has suggested that this reaction could be detrimental for HA densification [1]. Thereby, the present study focuses on understanding and fully characterizing the impact of the carbonation on the HA sinterability. To this end, the carbonation reaction could be modulated through (i) the initial A-site chemical composition of the powder (i.e. ratio of OHOH, CO3-OH, V+OH) and (ii) the partial pressures of H2O and CO2 in the sintering atmosphere.

HA and A-type CHA powders with variable ratio of OHOH / VOH and OHOH / CO3OH were prepared and carefully characterized by X-ray diffraction, infrared spectroscopy and thermal analysis. Then they were shaped into pellets by means of isostatic pressure. Their sintering behavior were fully characterized under 100 kPa He, 100 kPa CO2 and under a mixed atmosphere composed of 98 kPa CO2 and 2 kPa H2O. First, dilatometric analysis were recorded from ambient to 1300°C for each composition and under each atmosphere. Then, the densification mechanisms were identified under non-isothermal conditions thanks to the temperature increment method. In addition, the grain growth was observed by scanning electron microscopy. Finally, the physico-chemical characterization of the ceramics was carried out by infrared spectrometry, X-ray diffraction and chemical analysis to follow-up the evolution of the A-site composition during the heat treatment.

The results confirm that under a CO2 gas partial pressure, higher temperatures are needed to sinter HA. The main and original statement is an acceleration of the densification kinetics when A-type carbonates are present in the initial powder, leading to denser ceramics. This could be explained either by (i) a higher content of vacancies in the initial powder, or by (ii) the reduction of the carbonation reaction while sintering, as suggested by (1). Identification of the densification mechanisms and grain growth observations are under progress. Further works will focus on studying the impact of carbonation on B-CHA sinterability.

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Keywords: Carbonation reaction, Sintering, Hydroxyapatite

ABS 510

RESORBABLE CERAMIC MATERIALS BASED ON CALCIUM MAGNESIUM PHOSPHATES FOR BONE REGENERATION

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Several aspects need to be taken into consideration for regeneration of bone tissue in reconstructive and corrective surgery and orthopedics is the implant cytotoxicity and sufficient porosity to allow the growth of blood vessels, nerve tissue and bone cells proliferation. Furthermore, bone remodeling process depends on complex signaling pathway between osteoblasts and osteoclasts and control mechanisms to achieve homeostasis of their growth and differentiation. Considering the inorganic part of human bone is mainly composed of hydroxyapatite (HAP: Ca10(PO4)6(OH)2) and whitlockite (WH: Ca18Mg2(HPO4)2(PO4)12) minerals, where the WH phase occupies up to 20–35% of total weight and it can recapitulate early-stage of bone regeneration through stimulating osteogenic differentiation, prohibiting osteoclastic activity, and transforming into mechanically enhanced hydroxyapatite (HAP)-neo bone tissues by continuous supply of PO4^{3}- and Mg2+ under physiological conditions. In this study, we are obtaining porous resorbable ceramic materials based on calcium magnesium phosphates. Such materials According to the laser granulometry of calcium magnesium phosphate, the nanoparticle are suitable for 3D printing where they have a dark gray color, due to the presence of decomposition products of ammonium acetate. The resulting composite (monomers / powder) structures in the form of a Kelvin structure were exposed to a temperature of up to 1200°C. The study of the metabolic activity of cells in the presence of extracts from the material showed that the materials are able to support the adhesion, spreading and proliferative activity of human mesenchymal stem cells. These samples of biomaterials are biocompatible and do not have a cytotoxic effect on mammalian cells. The resulting ceramic materials are suitable for the creation of resorbable bone implants, including individually designed inorganics bases for the treatment of bone defects.

Acknowledgement: This work was supported by the RFBR, grant nos. 18-29-11079 and 18-53-00034.

Keywords: osteoconductivity, calcium magnesium phosphate,3D printing

ABS 483

MATURATION OF BIOMIMETIC HYDROXYAPATITE IN CELL CULTURE MEDIUM

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Objective Biomimetic calcium deficient hydroxyapatite (CDHA) exhibits exceptional osteoinductive and osteogenic properties, due to its high reactivity[1]. However, this is in contrast with its in vitro cytotoxicity, associated with the strong ionic exchange with the cell culture medium, and is amplified in static conditions[2]. The ionic fluctuations in the culture medium suggest that the material itself undergoes structural and physicochemical changes when in contact with physiological fluids. The purpose of the current work was to investigate in detail these changes.

Materials & Methods CDHA discs consisting of an entangled network of needle-like (fine) and plate-like (coarse) crystals were obtained by hydrolysis of alpha-TCP powders with fine and coarse particle size respectively. The specimens were consolidated by immersion in water at 37°C over 10 days. Subsequently, the discs were incubated in complete Advanced Dulbecco's Modified Eagle's Medium supplemented with 10% foetal bovine serum, 2 mM L-glutamine, penicillin/streptomycin and 20 mM HEPES buffer over extended periods of time of up to 50 days. The local chemical changes over increasing incubation times were determined using advanced confocal Raman microscopy and grazing incidence X-Ray diffraction (GIXRD), the microstructure by scanning electron microscopy and the Ca/P and Mg/P ratios were measured by inductively coupled plasma mass spectrometry (ICP-MS).

Results As indicated by Raman spectroscopy, the increased incubation times resulted in carbonation of the CDHA samples. A descending gradient of carbonation was observed from the surface to the core of all the specimens (Fig. 1). The carbonate incorporation was proved to be highly dependent on textural properties, with the effect being stronger for fine specimens. Furthermore, according to ICP-MS, an incorporation of calcium and magnesium ions occurred in the samples incubated longer times in the culture medium. The effects were more profound for the fine discs. No differences in the microstructure or crystalline phases on the surface were observed during extended incubation times for neither fine nor coarse samples.

Conclusions The ionic exchange with the physiological fluids results in gradual changes in the material, increasing its similarity to the bone mineral phase. This process is strongly modulated by the textural properties of the material.

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[2] *J.M. Sadowska et al. Acta Biomater. 76 (2018) 319-332.*

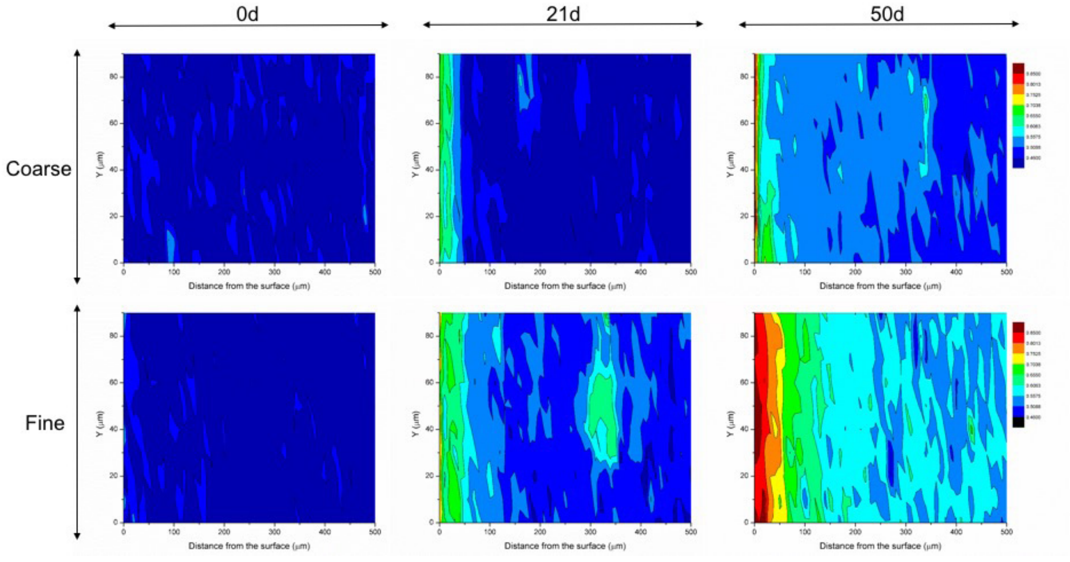

Figure 1. Raman microscopy mappings of carbonate content gradient from the surface to the inside of the CDHA discs (coarse and fine cross-sections) over different incubation times in the culture medium.

Keywords: Calcium phosphates, Biomimetic hydroxyapatite, Confocal Raman microscopy

ABS 474

COMBINING FLAME SYNTHESIS AND ADDITIVE MANUFACTURING TECHNOLOGY FOR THE PREPARATION OF NOVEL ÅKERMANITE SCAFFOLDS

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The investigation here presented was essentially aimed at providing a new, glass-based strategy for the development of Åkermanite (Ca2MgSi2O7) bioceramics, with distinctive control of porosity. The amorphous state is important, for the preparation of 3D-printed scaffolds, since the sintering process can start at a processing temperature Tx, much lower than that required for ceramic powders, in the window T = Tx – Tg, where Tg is the glass transition temperature. Åkermanite and other similar systems are difficult to prepare by conventional melt quenching method in fully amorphous state, due to the high crystallization rate. However, fully amorphous solid glass microspheres (SGMs), with a diameter 5-60 μm, were successfully prepared by means of flame synthesis, applied on an Åkermanite glass-ceramic precursor, previously obtained by traditional melting process. Once mixed with a photo-curable acrylic resin the microspheres were used for digital light processing, the glass sphere led to highly regular reticulated scaffolds. Finally, after burn-out of the organic binder, sintering at 900-1100°C led to scaffolds combining both macro-porosity from 3D printing and micro-porosity from the 'freezing' of viscous flow operated by intensive crystal precipitation, possessing a remarkable strength-to-density ratio.

Keywords: Akermanite, Flame synthesis, Glass microspheres

ABS 451

MULTIFUNCTIONAL MAGNETIC CALCIUM PHOSPHATE AND SILICA BASED NANOCOMPOSITES FOR BREAST CANCER THERAPY

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Breast cancer diagnosis and treatment improved significantly in last decade, with many available therapeutic strategies as surgery, radiation, chemotherapy, hyperthermia, immunotherapies and targeted therapies. However, some breast cancer such as triple negative breast cancer remain incurable and all these techniques present limitations and disadvantages. Nanoparticles are pointed as new strategies for selective therapy. It is proposed a new approaches to treat and monitor cancer by developing hydroxyapatite (HAP) magnetic nanoparticles and mesoporous silica coated iron oxide nanoparticles to be used as drug nanocarriers, contrast agents for magnetic resonance imaging (MRI) and hyperthermia agents. Synthetic hydroxyapatite based on micro- and nano-systems is used in medical field due to its excellent biocompatibility and non-inflammatory properties. The high stability and flexibility of apatite structure allows an easy incorporation of magnetic ions. Taking all these issues into account hydroxyapatite based magnetic nanoparticles (HA-MNPs) were prepared by a wet chemical precipitation method doped with different metal ions. Results showed that the particles prepared present a rod-like shape with sizes in a nano-range. It was shown that the doping concentration with respect to the atomic percentage of $Ca2+$ does not significantly alter the HAP structure although it has a predominant role in the magnetic properties of the nanoparticles. The results achieved in the present project suggest that the nanoparticles produced seems to have potential for medical applications in the future as a versatile MRI contrast and hyperthermia agent. Regarding the mesoporous silica coated iron oxide nanoparticles, this work proposes an optimized Stöber method to coat magnetite based nanoparticles with silica in order to improve their biocompatibility, with the further possibility to functionalize the silica coating. Results showed that nanoparticles were homogeneous regarding chemical composition, silica layer thickness, total size and morphology. By simply varying the reaction parameters pore sizes, surface area and pore volume could be adjusted for enhanced loading and release of anti-cancer drugs. The present work proposes a strategy that combines therapeutics and diagnosis on a single platform that will allow surpassing active cancer drugs poor specificity and dose-limiting toxicities during chemotherapy.

Keywords: Cancer Therapy, Hydroxyapatite, Silica

ABS 449

IMPORTANCE OF GRAIN ORIENTATIONS FOR THE CHEMICAL STABILITY OF BETA-TRICALCIUM PHOSPHATE CERAMICS

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Among the family of synthetic bone graft substitutes, β-tricalcium phosphate (β-TCP) has received much attention due to its chemical similarity to bone mineral, its osteoconductive properties and its osteoclast mediated resorption. Studies on β-TCP resorption by osteoclasts generally showed "dissolution pits" [1] on the surface of resorbed grains, suggesting a preferential crystallographic orientation for resorption. However, this correlation was not confirmed yet. Hence, in this study, we aimed to test the hypothesis that β-TCP dissolution/resorption is a crystallography-driven process. Pure calcium deficient hydroxyapatite (CDHA) with a Ca/P molar ratio of 1.50 was synthesized via an aqueous precipitation method using ultrapure raw materials. Then, CDHA was converted into β-TCP by a thermal treatment (1 h, 850°C). Dense β-TCP cylinders were obtained by subsequent powder milling, slip casting and sintering (3 h, 1100°C). Phase purity and content of chemical impurities were measured by X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Dissolution experiments were conducted in an acidic NaHCO3-HCl solution (pH 4.4) during 1 h whereas resorption experiments were realized in primary cell derived osteoclast cultures for 24 h. Dissolved and resorbed grains were imaged by scanning electron microscopy using secondary electrons (SEM-SE) and grain orientations were assessed by electron backscatter diffraction (EBSD). All samples were made of phase pure β-TCP, with low amount of impurities (maximum: 30 ppm for Sr). EBSD measurements revealed no preferential grain orientations. After dissolution or resorption, some grains were etched and showed the characteristic "dissolution pits" on their surfaces. EBSD acquisitions correlated their crystalline orientations with the c axis of the β-TCP crystal structure (Figure 1). The most pitted grains were those whose c-axis was oriented normally to the sample surface. Thus, this study highlighted that pure β-TCP dissolution/resorption is a crystallography driven process which occurs preferentially along the axis of the lattice parameter c of the β-TCP crystal.

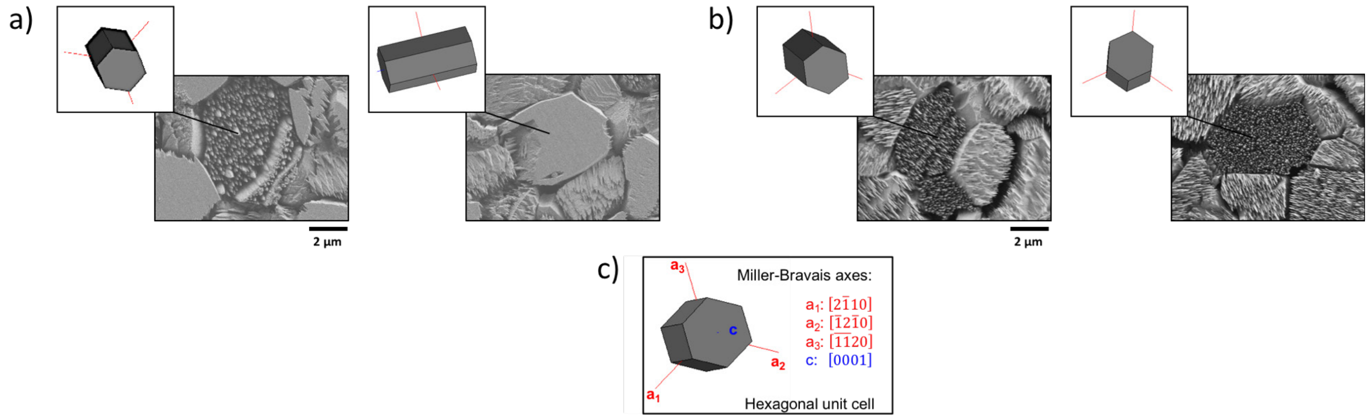

Figure 1: Correlation between dissolution pits and the β-TCP crystal orientation: (a) After 1 hour of dissolution in NaHCO3-HCl; (b) After 24 hours of resorption by osteoclasts; (c) Hexagonal unit cell of the β-TCP crystal.

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Acknowledgments The would like to thank the Swiss National Science Foundation Funding (grant n°200021_169027) and the European Commission funding of the 7th Framework Program (ITN grant n°289958, Bioceramics for bone repair).

Keywords: beta-tricalcium phosphate, grain orientation, dissolution, resorption

ABS 415

TURNING ZIRCONIA FROM STRUCTURAL TO AESTHETIC BIO- AND STRUCTURAL CERAMICS FOR RESTORATIVE DENTISTRY

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To repair damaged and/or missed teeth requires materials that can bear the bite force, is at least biocompatible if not bioactive, and preferably appears aesthetic as natural teeth. Zirconia ceramics was selected as the top candidate for this purpose a decade ago. As a typical structural ceramics with the highest fracture toughness in the category of ceramics, zirconia ceramics has conventionally been developed for structural purposes such as engine components and ceramic bearings. To meet the clinic demands of restorative dentistry more functions have to be added into the zirconia ceramics that otherwise is opaque white and bio-inert. In this presentation, we will describe how the optical behaviors of zirconia ceramics, e.g. translucency, brightness, colors and shades can be manipulated, so does the bio-behaviors, e.g. the potential integration with soft and hard tissues, respectively, by tailoring its hierarchical structures, particularly the surface topographic features in multiple scale of nano- and micrometers. Additional concern of the performance variations brought in during the production of customized components by either subtractive or additive manufacturing processes will also be discussed, with the focus on the minimization of processing defects, on the maximization of density and on the optimization of surface the surface topographic features.

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Keywords: Zirconia, Bio-ceramics, Microstructures

ABS 414

RELEVANCE OF BETA-TRICALCIUM PHOSPHATE IN VITRO BIOACTIVITY TO INTRINSIC OSTEOINDUCTION

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Introduction Intrinsic osteoinduction of calcium phosphate biomaterials is a phenomenon that remains unclear with regard to its mechanism. It is mostly observed with calcium phosphates such as beta-tricalcium phosphate (β-TCP), hydroxyapatite, or their combination but not exclusively[1]. Recently a new concept relating the ability to form an apatite layer onto the surface of the material (also called bioactivity) depleting locally the environment of Calcium and inducing a pH decrease was described as the first step in the material induced ectopic bone formation[1]. Fine tailoring of processing and composition parameters can produce bioactive biomaterials with optimal osteoinductivity[2].

Objectives The objective of this study is to correlate the bioactivity in a simulated fluid (SBF), with the intrinsic osteoinductivity of a set of different β-TCP samples.

Material & Methods A four factors two-levels factorial design was defined. Particle size (S=fine, coarse), calcium to phosphorus ratio (Ca/P= 1.5, 1.51) sintering temperature (T°= 900°C, 1100°C) and porosity (P= high, low) were varied to produce 16 types of β-TCP granules with all possible combinations of factors. A mass of 0.3g of material was introduced in 200ml of 1.5X SBF and pH and calcium concentration were monitored every seconds during 18 hours. Samples were then observed by SEM.

Results Calcium concentration and pH decreased following an exponential decay pattern (Figure 1) due to the precipitation of calcium deficient hydroxyapatite (CDHA) on the surface of the material following equation 1.

Precipitation reaction was monitored accurately and kinetics of calcium and pH decrease were affected by the different processing and composition of β-TCP granules. A faster precipitation occurred with smaller particles, higher Ca/P, higher porosity and lower sintering temperature. All samples exhibited a deposition of CDHA when observed by SEM (Figure 2). The magnitude and extent of CDHA crystals presence on the surface was correlated to the kinetics and levels of Ca and pH variations.

Conclusion Bioactivity can be monitored in vitro with in situ Ca and pH measurements, processing and composition of β-TCP granules affected their bioactivity. This novel and fast biomaterial screening technique opens up new perspectives towards linking the physicochemical phenomena with intrinsic osteoinduction.

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Keywords: Osteoinduction, Bioactivity, Beta-tricalcium phosphate

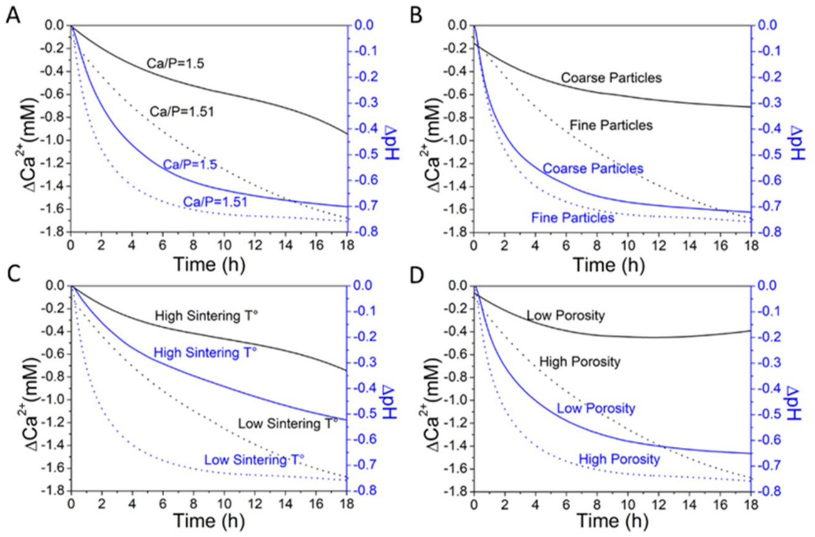

*Figure 1- **Calcium (in black)** and **pH (in blue)** variation curves for selected β-TCP samples. Same β-TCP sample is taken as reference in all 4 graphs (S=Fine, Ca/P=1.51, T°=900°C, P=High) and the paired comparison is made with another material varying one factor at a time, A) Ca/P, B) Particle size, C) Sintering temperature, D) Porosity .*

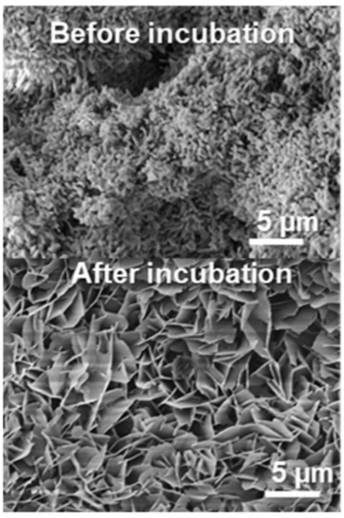

Figure 2- SEM micrograph of the reference sample used in figure 1 before and after 18h of incubation in 1.5x SBF.

Equation 1-

$$9\mathrm{Ca}^{2+} + 6\,\mathrm{HPO_4}^{2-} + \mathrm{H_2O} = \mathrm{Ca_9(HPO_4)(PO_4)_5OH} + 6\mathrm{H}^+ \quad (1)$$

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3D PRINTING OF BONE SUBSTITUTE MATERIALS BASED ON CAPILLARY SUSPENSIONS

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Additive manufacturing technologies such as 3D printing of bone substitute materials attracts more and more attention as it makes porous bodies with adjustable geometries and controlled material properties readily available.

We successfully transferred the recently presented processing route for manufacturing highly open porous, hierarchically structured ceramics via direct ink writing (DIW) of Al2O3 [1] to β-tricalcium phosphate (TCP) with incorporated nanoparticles and barium titanate. Both ceramics to be used for bone substitute materials. This manufacturing concept is based on the capillary suspensions concept [2], i.e. the ink consists of particles, a bulk fluid, and a small fraction of an immiscible secondary fluid. The secondary fluid induces the formation of a sample spanning network serving as pre-cursor for the porous sintered and also provides the characteristic shear thinning and yield stress necessary for the DIW process. Here, the composition of the ink, the debinding and sintering process had to be adjusted according to the distinct wetting and surface properties of the used particles.

We manufactured log-pile structures to be used as porous bone scaffolds and characterized them with respect to their pore structure (porosity, pore size) using SEM and mechanical strength employing compression tests, respectively. The printed specimen consisted of fully open-porous struts with porosities between 45 and 60% and strut pore sizes $x_{50,3}$ = 6 µm, the total porosity of the cellular structure reached up to 88%. The log-pile samples had printed pore sizes between 50 and 500 µm and strut width with a minimum of 150 µm. The samples without nanoparticles showed a max. compressive strength of 20 MPa. With incorporation of nanoparticles the samples strength was increased by 50%.

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Keywords: Capillary Suspension, Open-porous ceramics,3D printing

ABS 372

FUNCTIONALLY GRADED CALCIUM PHOSPHATE MATERIALS: EFFECT OF PROCESSING PARAMETERS ON STRUCTURAL AND MECHANICAL FEATURES

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Calcium phosphate bioceramics with chemical composition close to biological bone are one of the most studied materials in orthopaedic applications. Although very good biocompatibility and bioactivity properties, unreliable mechanical properties limit the application of these materials to non-load bearing sectors.

The final mechanical properties of ceramics are mainly governed by sintered density and grain size. The higher the final density, the lower the residual porosities and the higher the mechanical performance. Densification during sintering is dependent on different processing parameters. Among them, the effect of the particle size distribution of the initial powder and sintering cycles on the final density and microstructural features of a commercial hydroxyapatite powder have been studied in this work. To this aim, particle size distribution of the powder was tailored using two different milling methods. Precisely, under dry or wet-milling conditions, powders with a range of size distribution were achieved. In the following step, the effect of different heating rates on the sintering behaviour of gelcast bodies produced from above-mentioned powders were evaluated and materials with different level of density, porosity and mechanical strength were produced. The final materials were composed of hydroxyapatite and beta-tricalcium phosphate, where these two phases were contained in different amounts depending on the processing parameters. It has been found that the particle size distribution has the most significant effect on the final density and it was not possible to produce dense bodies if the average particle size was higher than a threshold value, set at 1 and 0.8 µm for 3 hour and 1 hour sintering at 1300°C, respectively. By sintering of the powders with low enough particle size distribution under moderate heating rates, it was possible to produce dense bodies with very low residual porosities and hence high mechanical properties.

Further aim of this work was the production of porous bodies using gel-casting combined with direct foaming method. Well sintered bodies, with a porosity in the range 40 – 85% were produced. Reduction of the residual pores in the struts, which results from the previously optimized sintering parameters, resulted in porous bodies with compression strength in the range of the cancellous bone.

Once optimized the processing parameters of both dense and porous bodies, functionally graded structures, characterized by both porosity and compositional gradients, were produced. These materials were design to provide both mechanical function, due to the dense core, and biological functions, due to the outer porous layer.

Keywords: Calcium phosphates, Functionally graded materials, Sintering

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3D PRINTED SCAFFOLDS BASED ON HYBRID BIOACTIVE SYSTEMS FOR BONE TISSUE ENGINEERING APPLICATIONS

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Nowadays, the significant number of bone fractures due to pathological conditions such as osteoporosis represents a relevant worldwide problem that is still unsolved. The current pharmacological treatments tend to increase bone mineral density and decrease osteoclast activity, without restoring the physiological balance between osteoblast (Ob) and osteoclast (Oc) activities that is crucial for a physiological bone remodelling [Torstrick et al., 2014]. For this reason, bone tissue engineering has been increasingly indicated as a valid solution to meet the challenging requirements for a healthy bone regeneration in the case of bone loss or fracture [Jakob et al., 2013]. In such a context, the ERC BOOST project aims at designing a 3D bio-extruded bioactive scaffold mimicking the chemical and structural properties of native bone to provide specific instructive signals able to direct and modulate a proper cell response. Firstly, a multi-scale study has been conducted on human bone samples (provided by Istituto Ortopedico Rizzoli, Italy) to define the main differences between healthy and osteoporotic tissues in terms of both mechanical and structural properties. With this aim, nanoindentation and compressive tests have been performed in addition to structural analyses using micro-computed tomography (micro-CT) and Raman spectroscopy. CAD/CAM models of healthy bone derived from micro-CT analyses have been optimised to produce high-resolution structures by means of a biofabrication platform, purposely developed at Centro Piaggio (University of Pisa, Italy), able to process different biomaterials. Hybrid bioactive systems, based on type I collagen and inorganic particles of strontium-added mesoporous glasses and nano-hydroxyapatite, have been developed and subsequently characterised in terms of physico-chemical and rheological properties, to verify their suitability for 3D printing applications. 3D printed structures have been obtained using the extrusion-based approach, to define the optimal printing parameters and conditions for 30 G needles. Different crosslinking methods have been investigated in order to better mimic the natural organisation of bone, while increasing the material stability exploiting the covalent bonds between collagen molecules. In addition, UV-induced crosslinking of methacrylate collagen has been properly optimised to maximise the efficiency of the process. Biological tests, carried out at Istituto Ortopedico Rizzoli and Università Politecnica delle Marche, showed the potential of the developed systems. For this purpose, both crosslinked and non-crosslinked material has been cultured in presence of human osteoblasts and osteoclasts.

Acknowledgement
This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 681798-BOOST).

Keywords: Bone Tissue Engineering,Hybrid Systems,3D Extrusion Printing

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TUNABLE NANOSYSTEMS FOR SMART DELIVERY OF BIOACTIVE MOLECULES DIRECTING CELL FATE

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The ever increasing need of more effective and targeted therapies for the treatment of cancer and various degenerative pathologies is pushing material scientists to develop new solutions associating enhanced safety with smart functionality, also permitting the establishment of personalized therapeutic approaches.

In this respect, the development and use of nanoparticles is today limited by several factors among which: i) low biodegradability and biocompatibility; ii) toxic by-products; iii) uncontrolled drug release into the bloodstream; iv) limited cell-target specificity and v) low efficiency in crossing biological barriers.

In this respect a novel apatite based nanoparticle (NPs) have attracted the attention of scientific community for biological and medical purposes as promising materials for drugs, genes or cells delivery, DNA/biomolecules separation, hypothermal treatment of tumours, contrast agents for imaging, and recently in tissue engineering and theranostic applications.

Recently, novel biomimetic, fully biodegradable and cytocompatible NPs fabricated at ISTEC-CNR by doping hydroxyapatite (HA) with Fe ions (FeHA), avoiding the presence of magnetic secondary phases and coating, were developed and biologically tested as new new drug delivery systems.

The wide possibility of surface functionalization of apatitic nanoparticles significantly extends the potential to develop smart drug carriers with active or passive ability to cross physiological barriers and to reach relevant organs such as the brain, the lung or the heart.

Keywords: Hydroxyapatite nanoparticles, Delivery systems, Cell fate

ABS 366

ALUMINA-ZIRCONIA COMPOSITES FOR DENTAL APPLICATIONS BY MICROSTRUCTURE DESIGN

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The idea of manufacturing artificial dental implants is not new. As for ceramic-made parts in oral surgery, alumina and zirconia have been considered since several decades ago, though a convincing consensus from the scientific clinical community has not been reached yet.

It is well known in fact that alumina is unable to confer enough fracture toughness to thin implant's sub-components. On the other hand, zirconia possesses the necessary fracture toughness but is prone to low temperature degradation (LTD).

A well-established approach is try merging into a newly designed composite the best requisites of each constituting member. For instance, the effort to improve at once fracture toughness, flexure strength and LTD yielded zirconia-toughened alumina (ZTA) and alumina-reinforced zirconia (ATZ) with optimized end members volumetric percentages. Nevertheless, materials for dental implants should have not only mechanical stability but also a pronounced bioactivity.

In view to gain an overall performance improvement in mechanical properties, bioactivity and LTD, microstructure functionalized alumina-zirconia composites for dental implants were specifically designed, manufactured and characterized.

Keywords: Alumina-Zirconia Composites,Dental Application,Microstructure Design

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DESIGN OF CALCIUM PHOSPHATE COATINGS FOR BIOMEDICAL APPLICATIONS USING THE ELECTROSTATIC SPRAY DEPOSITION TECHNIQUE

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Replacement of missing or diseased hard tissues has become a common procedure in medicine and dentistry. In this field, coatings are frequently applied onto the surface of metallic implants, such as titanium and titanium alloys in order to improve their biological performance -i.e., to enhance bone contact or bone anchorage, defined as osseointegration-. Because of their similarity to the inorganic component of bones and teeth, calcium phosphate (CaP) ceramics are considered as a suitable material for use as a surface coating.[1]

Currently, the most frequently applied method to coat titanium implants with CaP films is the plasma spraying technique, which has considerable drawbacks, for instance, unpredictable phase changes, the large thickness needed to completely cover the implant, and possible particle release and delamination.[2,3] Among alternative methods of depositing CaP coatings, Electrostatic Spray Deposition technique (ESD) is investigated as a promising low temperature deposition technique.

ESD is a low-cost method, innovative, based on electrohydrodynamics' laws, that allows the deposition of films with a large variety of original morphologies and phases including crystalline and amorphous states of CaP. In this study, the microstructural and structural properties of the CaP coatings deposited on Ti alloy are investigated for different precursor solutions containing calcium and triethyl phosphate and for several ESD deposition parameters. The microstructure and composition of the obtained coatings were characterized by scanning electron microscopy (SEM) associated with energy dispersive X-ray spectroscopy (EDX). Their structural properties were determined using X-ray diffraction (XRD), Raman spectroscopy and Fourier-transformed infrared spectroscopy (FTIR).

This work [4] has shown that ESD proved to be a viable and potentially interesting technique to coat pure calcium phosphates such as carbonated hydroxyapatite on metals (Ti alloy) with unique dense, reticular or coral-type microstructures. Moreover, CaP films appear to be adherent and osteoconductive. The biological coating performances in vivo and in vitro studies are in progress.

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Keywords: Electrostatic spray deposition, Carbonated hydroxyapatite, Dental and orthopedic implants

ABS 318

SINTERING OF SODIUM AND POTASSIUM TCP BASED CERAMIC FOR BONE GRAFTING APPLICATION

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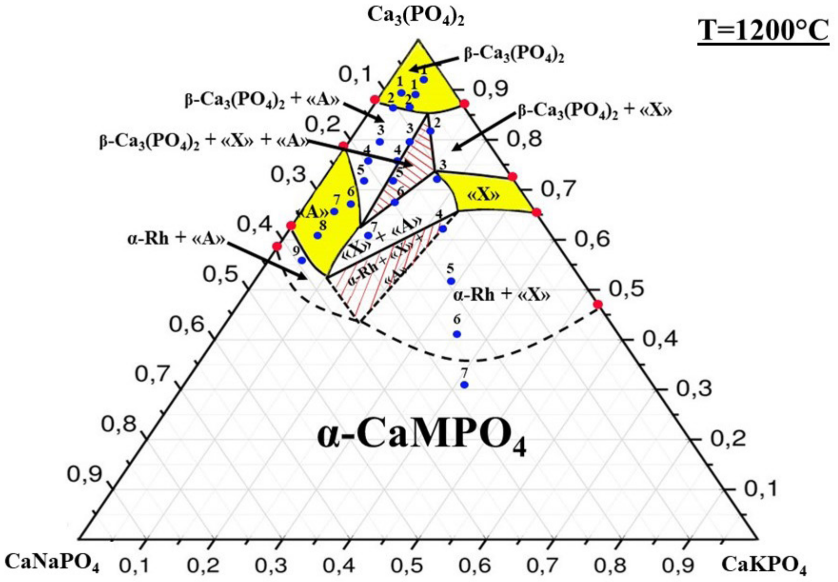
Biomaterials for bone replacement and grafting should possess sufficient strength, be bioresorbable and demonstrate osteoconductive and osteoinductive properties. However, resorption of modern materials for bone grafting(hydroxyapatite (HA) and tricalcium phosphate (TCP)) is reported, in some cases, to be not enough, this is why the search for more soluble compounds compared to HA and TCP looks very perspective. A possible way to increase ceramics solubility leads to partial substitution of Ca2+ -ions in Ca3(PO4)2 by alkali cations, like Na+ or/and K+. Improvement of solubility stems from decreasing lattice energy of a substituted phase, as well as the increase in hydration energy of the ions releasing from the phase to ambient solution. From this viewpoint, bioceramics based on compositions from Ca3(PO4)2 - CaKPO4 - CaNaPO4 ternary system seems to be prospective for bone replacement and grafting in the sense of resorption properties. At the same time, one should bear in mind that solubility level (resorbability) is governed not only by reduction of lattice energy but also by microstructure features. Grain sizes and porosity contribute much to dissolution rate making the study of sintering of the ceramics mentioned above highly important.
To control Ca3(PO4)2 - CaKPO4 - CaNaPO4 based ceramic microstructure it is necessary to know possible phase transformations in the system and the way to manage microstructure by sintering schedule or sintering process.
In this work, an isothermal section for phase diagram of Ca3(PO4)2 - CaKPO4 - CaNaPO4 ternary system is studied with several techniques. According to the XRD of quenched samples, this phase triangle has four single-phase areas at 1200°C (Figure 1). It was shown that single-phase CaK0.6Na0.4PO4 cannot be sintered to full-dense ceramics by conventional sintering regardless time-temperature schedule. Two-step sintering technique, beneficial in the case of HA-ceramics, was unsuccessful in all cases of calcium-alkali phosphate compositions. However, field-assisted sintering techniques like e.g. Spark Plasma Sintering (SPS), can overcome this problem due to significant impact on grain boundary diffusion. In connection with this fact, grains grow much slower retaining sintering process in a pore control regime. In this work CaK0.6Na0.4PO4 low-porous ceramics was also fabricated by FAST-methods of sintering. Moreover, other alternative sintering techniques, such as reaction sintering, may be useful in accelerating ions diffusion but stopping excessive grain growth.
Strength properties of ceramics were evaluated by B3B-testing, micro- and nanoindentation techniques. Fracture toughness also becomes higher with potassium content increase, guiding porosity level.
Resorption properties of sintered ceramics were studied in different solutions with pH=5 and 7.4.

Acknowledgements The research of sintering processes in calcium phosphate materials was funded by RFBR according to the research project #18-33-00974.

Keywords: Calcium phosphate ceramic, Phase diagram, Mechanical properties



ABS 306

3D BIOCERAMIC MICROENVIRONMENT TO GUIDE MESENCHYMAL STEM CELLS AND ENDOTHELIAL CELLS IN BONE TISSUE REGENERATION

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Objective An emerging concept in material science is to draw inspiration from natural processes and products, which we may consider as the most advanced examples of smart nanotechnology. Natural structures such as woods and plants exhibit multi-scale hierarchic organization that is the source of smart and anisotropic mechanical properties associated with high porosity and lightness. Porous woods (rattan) were recently transformed into hydroxyapatite (HA) scaffolds with hierarchic organization focusing on long bone critical defect.

Methods & Methods The whole chemical conversion of rattan wood has been carried out through five steps from native wood to porous HA1. HA-based scaffolds, already commercially available as a biomimetic bone graft were used as control group.
Human adipose-derived mesenchymal stem cells (ADMSCs) were cultured on the 3D samples in birectional perfusion conditions in combination with human umbilical vein endothelial cells (HUVEC) up to 4 weeks in a perfusion bioreactor system (Cellec Biotek AG). Cell viability, cell morphology, protein and gene expression profile were analyzed.

Results A very high ratio of viable cells was seen with no significant differences between the innovative scaffold and the commercial sample. Microvessels within the 3D microenvironment were detected. The morphological analysis showed ADMSCs grown into the porous scaffold structure remaining firmly attached to the samples surface. The investigation of the expression of proteins and genes involved in the osteogenic differentiation highlighted a significant effect of the bioinspired sample on the up-regulation of the genes involved in both early and late stages of osteogenic commitment if compared to commercial sample.

Conclusions This study demonstrated that 3D scaffold obtained by biomorphic transformation, with already proved high mechanical performance, strongly enhanced the interaction between endothelial cells and mesenchymal stem cells. This achievement is pivotal for a closer mimicry of the complex 3D bone structure and composition which can drive and direct the regenerative cascade at the cell level, towards the regeneration of extensive load-bearing bone parts.

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Keywords: Cell/materials interactions, Biological evaluations, Co-culture

ABS 271

MULTI-DOPED BIOMIMETIC APATITES WITH ENHANCED ANTIBACTERIAL AND OSTEOGENIC PROPERTIES

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The development of cell-instructing biomaterials with ability to promote and sustain bone regeneration is today a hot research topic, in consideration of the steady increase of bone diseases, including traumas, cancer or other degenerative diseases involving extensive tissue loss, among the world population.

A serious concern in this field is the relatively frequent occurrence of intra- or post-operatory infections which can seriously impair the therapeutic effectiveness and the healing process.

An approach could be the use of multifunctional biomaterials associating inherent therapeutic and anti-infective ability, which may represent a smart tool to improve clinical outcomes while providing locally targeted inhibition of infective processes.

In this respect, in the present work, single phase, nanocrystalline apatite powders are prepared for the first time by simultaneous co-doping with Ga3+, Zn2+, Mg2+ and CO32- ions, selected for their ability to increase osteogenic and antibacterial ability in respect to non-doped.

Single- and multi-doped, with Zn2+,Ga3+, Mg2+ and CO32- HA, were synthesized by a neutralization method in aqueous environment. The synthesis process was carried out at 40 °C to limit the crystal development in the final apatite phase.

Nanocrystalline apatite powders co-doped with Ga3+, Zn2+, Mg2+ and CO32- ions, selected for their ability to increase osteogenic and antibacterial ability in respect to non-doped and single doped Ga-apatite and Zn-apatite, as assessed by culture of human mesenchymal stem cells and of four different pathogens selected among the most frequently occurring in nosocomial diseases. In particular, the co-doping with Mg2+ and CO32- enhances human stem cells proliferation and expression of genes relevant for bone regeneration and, at the same time, yields stronger reduction of bacterial proliferation after 24 hours. With this, multiple ion doping of hydroxyapatite reveals as a promising way to obtain multi-functional biomaterials giving effective and sustained bone regeneration whereas strongly reducing post-surgical infections, which are major causes of therapy failure when bone implants or scaffolds are used.

Multiple ions doping in the hydroxyapatite structure provides multifunctional ability of enhanced osteogenic and antibacterial properties, against various bacterial strands common in post-operatory infections. Particularly, it is shown that the co-doping with Mg2+ and CO32- enhances the osteogenic character of hMSCs and the antibacterial effects of ions such as Ga3+ and Zn2+.

The new apatites are then promising as materials for bone substitution or for osteointegrative, antibacterial coatings on prosthesis to improve the clinical outcome and reduce revision surgery.

Keywords: hydroxyapatite, antibacterial, osteogenic

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STRONTIUM/CARBONATE CO-SUBSTITUTED TWO-PHASE SYSTEM OF HYDROXYAPATITE AND OCTACALCIUM PHOSPHATE DERIVED FROM CUTTLEFISH BONE

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Objective Hydroxyapatite (HAp) is the most widely used calcium phosphate (CaP) for hard tissue applications due to its compositional similarity to biological apatite, biocompatibility and bioactivity. Along with HAp, octacalcium phosphate (OCP) and tricalcium phosphates (TCP), are gaining increasing attention. As bone apatite is a multi-substituted carbonated HAp containing trace elements, one of the used approaches to improve the biological and physicochemical properties of CaPs is ionic substitution.

Materials & Methods In this study Sr-substituted CaPs, with varying strontium content (0, 1, 5 and 10 mol%), have been prepared by using cuttlefish bone as precursor of calcium and various trace ions. The effect of the doping on phase composition, crystal structure, morphology and thermal stability of synthesized materials was studied. Mineralogical composition of the as-prepared and the heat-treated powders were determined using X-ray diffraction analysis. The lattice parameters, the cell volume and phase composition of prepared powders were determined by Rietveld refinement using software DIFFRAC.SUITE TOPAS V.5.0. Ion release test was studied during 7 days of incubation in simulated fluid (SBF) at 37 °C. The chemical composition of as-prepared unsubstituted and Sr-substituted CaP powders, and concentration of released ions were determined by inductively coupled plasma mass spectrometry.

Results The precipitated powders were composed of HAp, OCP and amorphous CaP. After heat treatment, crystalline phase of TCP was detected. Along with strontium, unsubstituted CaP is doped with carbonate, sodium and magnesium ions, as they are present in cuttlefish bone. Sr-substituted CaP systems have similar trace element content (sodium and magnesium) as unsubstituted CaP system. CaP systems are carbonate substituted by B-type substitution as in natural bone mineral. Obtained results revealed an increase of cell volume ($Å^3$), lattice a-axis (Å), lattice b-axis (Å) and c-axis (Å) for all obtained CaP phases (OCP, HAp and TCP), due to larger ionic radius of strontium (1.12 Å) in comparison to substituted calcium (0.99 Å) ion. Strontium ions are located at Ca1 site in hydroxyapatite, Ca3, Ca4, Ca7 and Ca8 sites in OCP and Ca1, Ca2, Ca3 and Ca4 sites in TCP structure.

Conclusions Obtained results have shown that two-phase system of OCP and HAp can be synthesised from biogenic source at mild conditions. As result of using biogenic source, prepared CaP system is co-substituted with magnesium, sodium and carbonate ions, along with strontium as target substitution ion. Determination of ion position and substitution mechanism is of great importance to understand in vitro ion release.

Keywords: calcium phosphate, strontium, Rietveld refinement

ABS 249

STABLE, TOUGH AND DUCTILE CERIA-STABILIZED ZIRCONIA BASED COMPOSITES AS AN ALTERNATIVE TO TITANIUM AND YTTRIA-STABILIZED ZIRCONIA CERAMICS FOR DENTAL IMPLANT FABRICATION

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Titanium (Ti) and its alloys have been used for long in dental implants fabrication because of their high strength, biocompatibility, good osseointegration and resistance to corrosion. However, Ti-based dental implants can be visible in the oral cavity (aesthetic issue), produce Ti particles that will be fixed in both soft and hard surrounding tissues (debris generation issue) or create immunological response and allergies (biological complications). Consequently, because of these drawbacks, yttria-stabilized zirconia (3Y-TZP) ceramics started to be used as an alternative to Ti implants. However, due to the possibility of 3Y-TZP aging (especially when the robustness of the whole ceramic processing step is low) and therefore to the risk of implant failure, alternatives to 3Y-TZP dental implants have been also developed.

In this work, a novel very-stable zirconia-based system is presented. These ceramics are composed of ceria-stabilized zirconia (Ce-TZP) and two second-phases, alumina (Al_2O_3) and strontium aluminate ($SrAl_{12}O_{19}$). During the oral presentation, the mechanical behavior (strength, fracture toughness, ductility and transformability) and aging resistance (Low Temperature Degradation) of these triphasic ceramics will be discussed and related to the microstructural features and/or composition (content of stabilizing agent and second-phases) and compared to Ti-based and 3Y-TZP materials. For some compositions, materials have exhibited a remarkable plasticity for a ceramic (strain~1%), very high Weibull modulus (m>60) and a low sensitivity to fatigue (fatigue limit of more than 90% of the tensile strength) which gives it an unneglectable advantage over the well-known 3Y-TZP ceramic.

The high flaw tolerance of Ce-TZP based ceramics and the predictive nature of the strength, associated to a transformation-induced plasticity and a perfect stability in-vivo allow us to consider them as the “new materials of choice” not only for dental implants (example here discussed) but also for other structural biomedical applications.

The research leading up to these results was undertaken in the framework of the LongLife project (www.longlife-project.eu grant agreement FP7/2007-2013 n. 280741) and the Siscera project (H2020-FTIPilot-2016, n. 737954), both funded by the European Community.

Keywords: Dental Implants, Ceria-stabilized zirconia, Mechanical behavior

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BIOACTIVITY ENHANCEMENT OF SILICON NITRIDE CERAMICS BY SURFACE OXIDATION

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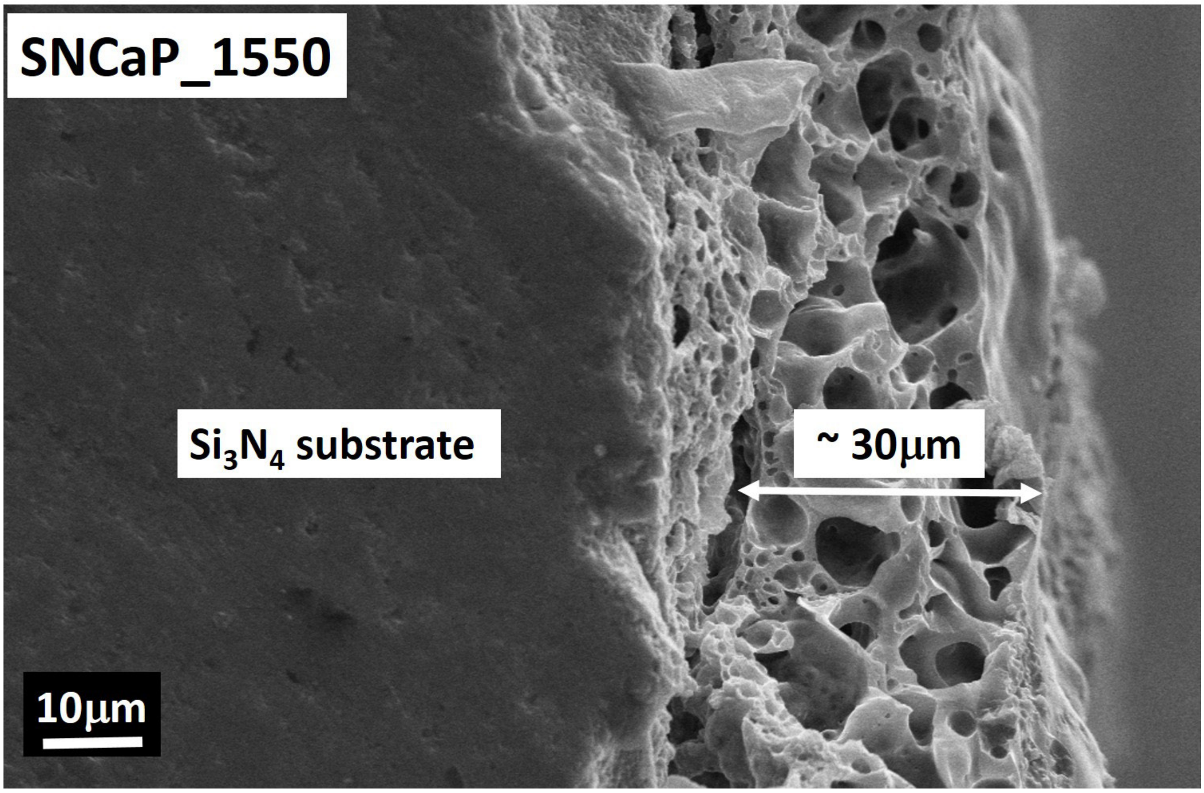
Silicon nitride is a covalent ceramic widely used in many structural applications due to its excellent mechanical properties, which result from microstructural features, i.e. interlocking of elongated β-Si3N4 grains. Despite its superior mechanical properties, silicon nitride seems to be an attractive implant material due to the biocompatibility and in vivo stability. Natural bioinertness of silicon nitride surface was switched to bioactive by modification of grain boundary composition and surface topography. The additions of SiO2, CaO and Ca3(PO4)2 was studied in order to aid the liquid phase sintering and enhance the surface bioactivity of the final materials. The main idea lays in the fact that silicon nitride oxidation is usually accompanied with the diffusion/flow of the phases located at the grain boundaries to the ceramic surface. Surfaces of studied silicon nitride based ceramics were treated by oxyacetylene torch in order to study the effect of this treatment as well as the effect of additives on final surface topography.

The surfaces of substrates after oxy-acetylene flame thermal treatment were covered by oxide containing and porous layer with thickness from 10 to 100 μm with respect to the sintering additive system. Wide pore size distribution, interconnectivity as well as irregularity of pore shape are result of the rapid evolution of gaseous products related to the decomposition of phases of substrate matrix. Formation of hydroxyapatite deposits on the surfaces after SBF (simulated fluid) immersions was studied, suggesting their bioactivity. The most enhanced bioactivity was observed in case of substrate with Ca3(PO4)2 as sintering additive.

Keywords: silicon nitride, surface modification, oxy-acetylene flame oxidation



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EFFECT OF STOICHIOMETRIC CALCIUM ZIRCONATE DOPANT ON THE DECOMPOSITION OF HYDROXYAPATITE

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Ceramic composites of hydroxyapatite reinforced by fully stabilized zirconia can combine the biocompatibility of HA with the high strength and fracture toughness of zirconia. However, the use of Y2O3 entails disadvantages particularly the phenomena known as “ageing phenomenon” related with its degradation even at low temperatures. Besides, the decomposition of HA into tricalcium phosphate (TCP) at 1300 ºC is also reported.

In this work, CaZrO3-HA composites obtained by rate controlled sintering were manufactured and the effect of stoichiometric calcium zirconate dopant (10 and 20 wt.%) on the decomposition of hydroxyapatite, microstructural, mechanical and biological properties were studied.

The results obtained showed that the addition of 10 wt.% of CaZrO3 to the hydroxyapatite allowed the production of biocomposites with lower theoretical density values (1.6 %), with a tensile strength and hardness for dense materials of the 55 MPa and 6.8 GPa, respectively. Moreover, the addition of CaZrO3 stabilizes the hydroxyapatite at least up to 1300 °C and inhibits the appearance of the alpha- and beta- TCP phases. The addition of higher values of CaZrO3 (20 wt.%) increases the porosity and does not improve the mechanical and biological properties of the biocomposite.

Furthermore, the in vitro assays demonstrated that the biocomposites of HA-CaZrO3 were biocompatibility, since they favoured human osteoblast cells adhesion and proliferation, in particular for the composition with 10 wt.% of CaZrO3.

These results highlight the potential of this ceramic composition for biomedical applications being an alternative to the traditional applications of hydroxyapatite.

Keywords: HA-CZ Biocomposites, Microstructural Properties, Biological Properties

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ULTRA-POROUS BIOCERAMIC MATERIALS WITH PREDEFINED ARCHITECTURE FOR BONE TISSUE ENGINEERING

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The regenerative approach in medicine requires the creation of tissue engineering constructs (TEC) for recovery of biological functions of damaged tissue. The basis of TEC in bone implantation is represented by biodegradable porous scaffolds, which are populated by bone-forming cells. The main properties of these scaffolds are biocompatibility, resorbability and osteoconductivity. Calcium phosphates are biocompatible due to the similarity with inorganic part of the native bone, and their resorption ability depends on the Ca/P ratio. Ideally, the material should have a resorption rate comparable to that of bone growth. Therefore, the most promising and useful calcium phosphate is tricalcium phosphate Ca3(PO4)2 (TCP).
Osteoconductivity of material for implantation is the ability to provide the bone growth and proliferation of blood vessels and nerves into the implant. Nowadays there is a well-established point of view that osteoconductive properties are characterized by the presence of the system of interconnected pores with a bimodal distribution: 1) the first mode – pores with the diameter more than 100 μm, to increase the permeability of biological streams into material, as well as the size of "connections" between such pores should be at least 50 μm, for the migration of the cells throughout material; 2) the second mode – pores with the diameter less than 10 μm, to increase the cell adhesion by increasing the surface roughness. At the same time, the total porosity should not be less than 50%.
To increase the permeability of the material, it is necessary to have an additional directed pore system in the form of straight channels (with a diameter at least 500 μm) in several directions; and the fraction of pores should be at least 70% of the total material volume. Creation of porous ceramic materials with high permeability is possible only using additive manufacturing. Stereolithography is one of the most universal and perspective methods, in which 3D-object is created using photopolymerization of individual suspensions.
The aim of our research activity is the creation of resorbable highly permeable ultra-porous ceramic scaffold based on tricalcium phosphate Ca3(PO4)2 with pre-defined architecture using the stereolithography method for bone tissue engineering.
In this work, we propose a new type of osteoconductive scaffolds, which have a more permeable specific architecture and accelerate the regeneration of native bone tissue. Such materials have ultra-porous (the porosity more than 85%) specific architecture with a complex (multimodal) system of pores of at least three levels.
Created ultra-porous ceramic scaffolds based on tricalcium phosphate demonstrate good resorbability and high osteoconductivity and can be used as a part of tissue engineering constructs in bone implantation.
The work was supported by RSF, grant # 18-79-00256. The acknowledge partial support from Lomonosov Moscow State University Program of Development.

Keywords: bioceramics, stereolithography, permeability

ABS 52

QUALITY ASPECTS OF ADDITIVELY MANUFACTURED MEDICAL IMPLANTS

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Rapid fabrication of individualized products is of special interest for the medical sector. Beyond research, only a few medical companies use Additive Manufacturing (AM) to fabricate medical end products. AM has advanced at a much faster pace than regulations or quality controls. The lack of standards and knowledge gaps in quality control makes companies waiting for more evidence of reliability to ensure patient safety before adopting the technology.

The European Metrology Programme for Innovation and Research (EMPIR) has set up a project to diminish these gaps. Validated techniques to verify the finished parts, thereby improving processes as well as reliability of the manufacturing chain are the objectives of the project, with the intention to increase the confidence of the medical device industry in the AM technologies. We will report about recent advances within the framework of the EMPIR project (Metrology for additively manufactured medical implants, MetAMMI).

Keywords: Additive Manufacturing, Medical Implants, Quality Assurance

ABS 43

SILICON NITRIDE DENTAL IMPLANT WITH ENHANCED BIOACTIVITY

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Titanium and its alloys are still the “gold” materials for dental implants. However, there is an increasing demand for metal-free dental restorations, which leads to the development of ceramic-based dental implants, such as zirconia. Except for zirconia, in orthopaedics, another ceramic, silicon nitride, has been used as the spinal implant and for joint replacement. Silicon nitride ceramics have been shown to have potential antibacterial properties besides their good mechanical strength. Regarding the dental implantology applications, good osseointegration is needed. An improvement of silicon nitride bioactivity could be essential to increase the osseointegration capability of the material. Our strategy is to add bioactive ions, such as Mg, Sr and Si, in silicon nitride ceramics. The aim of this study was to increase its bioactivity without sacrificing the mechanical strength and antibacterial properties. The new Si3N4 ceramics were sintered by SPS, followed by the analyses of mechanical strength, ion release, bioactivity, cytotoxicity, and antibacterial properties. The results were promising, and the bioactive silicon nitride ceramic could be of great interest for the use as dental implants.

Keywords: Dental implant, Silicon Nitride, Bioactivity

ABS 34

ATOMISTIC SIMULATIONS OF ADSORPTION FREE ENERGY OF AMINO ACIDS AT THE RUTILE (110)/WATER INTERFACE USING METADYNAMICS – IMPLICATIONS FOR SIMULATED FLUID BIOACTIVITY TESTS FOR MEDICAL IMPLANTS

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Single amino acids are present in blood plasma and are the building blocks of larger organic residues. Their interaction with surfaces is therefore crucial for biomedical applications in contact with blood or saliva. In this work, we use well-tempered metadynamics to study the adsorption of six amino acids, with non-polar (Ala and Leu), polar (Ser), positively charged (Arg and Lys) and negatively charged (Asp) side groups, on a negatively charged rutile (110) surface. The free energy of adsorption and the desorption rates were determined for all amino acids under different adsorption conformations. When using the center of mass as the collective variable in well-tempered metadynamics, results for different amino acids were difficult to interpret due to different adsorption conformations on the surface overlapping in collective-variable space. After projecting onto separate collective variables for the backbone and the side group much clearer trends were observable. We show that, on the negatively charged surface of rutile, adsorption via the backbone occurs for all the amino acids irrespective of their side group. Adsorption driven via the side group only occurs for polar and charged side groups as opposed to the non-polar side groups. This points to the importance of interactions of the side group with the strongly structured water layer rather than direct side group-surface interactions in determining the adsorption behavior. [1]

Such adsorption can interfere with the formation of hydroxyl apatite during in vitro bioactivity tests using the simple inorganic Simulated Fluid proposed in the ISO 23317 standard protocol. Experimental studies are also being carried out on the standard SBF system in the presence of amino acids to see if the atomistic simulation predictions can help understand the effects of such interfacial phenomena, as observed when proteins such as bovine serum albumin (BSA) are added to the SBF solution [2]. Also further experimental and molecular dynamic simulations are being carried out on the possible interference of the organic buffering agent, tris (hydroxymethyl)aminomethane (Tris), used in the current ISO standard test.

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Keywords: simulated fluids, amino acids, molecular dynamics

ABS 27

EXAMINATION OF ELECTROSPRAYED BIOGENIC HYDROXYAPATITE COATINGS ON SILICON NITRIDE AND CARBON NANOTUBE REINFORCED SILICON NITRIDE COMPOSITE

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Silicon nitride (Si3N4) bioceramic has very good mechanical and biological properties, therefore it is an excellent implant material for total knee and hip replacements [1-2]. There is no chemical reaction between bioinert ceramics (e.g. Si3N4) and the living tissue, however bioactive materials (e.g. hydroxyapatite) could induce tissue reactions in human [3]. Using a biodegradable and bioactive temporary nanohydroxyapatite (nHA) coating on the Si3N4 implant's surface could induce chemical bonds with the tissue, and fasten the healing process. The aim of this study was to produce nHA coating on silicon nitride (Si3N4) and carbon nanotube reinforced silicon nitride composite (Si3N4/CNT) substrates with electrospray deposition method.

Si3N4 and Si3N4/CNT substrates were produced by hot isostatic pressing [4]. The raw material of hydroxyapatite was crushed eggshell. Heat treatment and milling process in phosphoric acid resulted in the 100-200 nm sized HA phase. Electrospray deposition technique was used for producing thin nanohydroxyapatite (nHA) and nanohydroxyapatite/polyethylene glycol composite (nHA/PEG) coatings. XRD, SEM-EDS and TEM methods were performed for the phase determination and characterization. Micro-scratch test was performed also for the adhesion evaulation of the different coatings.

The coatings were non-uniform on the Si3N4 surface, and did not form a continuous layer due to the high electrical resistance. On the other hand, 4-5 µm thick porous nHA and non-porous nHA/PEG coatings were formed on the Si3N4/CNT substrate. According to the micro-scratch test results, the nHA/PEG layer has better adhesion (better resistance to scratching) and less fragile than the pure nHA layer.

Continuous nHA and nHA/PEG coatings were produced on Si3N4/CNT substrate with electrospray deposition method for biomedical applications. Micro-scratch test results revealed that the mechanical properties of nHA layer was improved by using PEG biopolymer.

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Keywords: hydroxyapatite, silicon nitride, electrospray deposition

ABS 16

RELIABILITY OF DIFFERENT ZIRCONIA CERAMICS FOR DENTAL RESTORATIONS AND IMPLANTS

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Ceramics being inherently brittle in general exhibit larger scatter in the strength values than metals, which may limit their use in structural applications. Thanks to the transformation toughening effect, zirconia ceramics can have higher toughness than other non-transformable ceramics and exhibit the highest strength of oxide ceramics. Along with the excellent biocompatibility and natural appearance, they are popularly applied and investigated for fixed dental prostheses and more recently for implants. Investigating their fracture behaviours and reliability is therefore a matter of great importance. In this work, we will present the strength distributions and Weibull plots of several zirconia (-based) materials that are aimed for dental applications.

In the case of restorative materials, the aesthetic requirement toward a higher translucency is driving the zirconia ceramics to be stabilized by a higher yttria content. We will discuss here three zirconia ceramics stabilized by 3, 4 and 5 mol% yttria in comparison to lithium-disilicate glass ceramic. Apart from the fact that the strength and toughness were lowered by increasing the yttria content, it was more striking that the reliability was also reduced due to a decreased crack-growth resistance for which the V-KI (crack velocity versus stress-intensity factor) diagrams under static and cyclic loading conditions were studied. 5 mol% yttria stabilized zirconia, being most translucent, exhibited similar toughness and strength but lower Weibull modulus than lithium-disilicate glass ceramic.

On the other side, for dental implants, the lower demanding on translucency opens the possibility of using alternative stabilizer and composite materials. A zirconia-based composite made of ceria-doped zirconia matrix with two second phases (alumina and strontium aluminate) could benefit from the transformation induced plasticity and thus resulted in very limited dispersion in strength data with exceptionally high Weibull modulus. For the system of yttria-stabilized zirconia, stabilizer content could be lowered from classic 3 mol% when the hydrothermal aging behavior was properly controlled by for example La2O3 doping. The combination of low yttria content (2 mol%) and 0.4 mol% La2O3 doping was able to realize a fairly stable alumina-toughened zirconia-composite with high crack-resistance (high fracture toughness and threshold from V-KI curve) and high reliability.

Keywords: Zirconia, Dental Materials, Reliability

S06

CERAMICS FOR ENERGY CONVERSION AND STORAGE

INVITED LECTURES

ABS 789

CERAMIC MATERIALS IN NUCLEAR WASTE MANAGEMENT

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The safe management of high-level radioactive wastes and ultimately their disposal in a deep geological repository is one of the grand challenges of our times. Various ceramic materials are involved in the back end of the nuclear fuel cycle, such as spent nuclear fuels from nuclear power plants, and ceramic and/or glass ceramic waste forms envisioned for immobilization of special radioactive waste streams. This presentation will provide an overview on these materials, focusing on two specific examples:

Nuclear fuels used in nuclear power plants are basically oxide ceramics based mainly on UO2 and (U,Pu)O2 (i.e. mixed oxide MOX fuels). SNF are complex materials due to their chemical and (micro)structural changes induced into the ceramics by the intense irradiation with neutrons during several years of service life in the reactor core. SNF includes fission products and trans-uranium/plutonium elements either in solid solution with the oxide matrix or on grain boundaries and in the gap between the fuel pellets and the cladding, and exhibit a complex microstructure. Despite this complexity, a sound understanding of the materials' behavior during interim storage (up to several decades) as well as in the repository environment (up to 1 million years) is required for safety assessments regarding the management and direct disposal of SNF. However, due to its complexity and its high radiation field, SNF is not suitable to gain mechanistic insights into all processes controlling its long-term behavior, e.g. regarding corrosion in the repository environment. Here, single effect studies on doped simplified UO2-based model materials allow for a refined understanding of, e.g., the effects of fission products, or Cr-doping, on the microstructure and the corrosion behavior.

Ceramic waste forms are considered for the immobilization of special waste streams such as separated plutonium, due to their specific properties including high structural flexibility, high chemical durability, and radiation resistance. In this context, pyrochlore-type and monazite-type ceramics have been studied, e.g., with respect to their atomic scale structure, radionuclide incorporation, and dissolution. A combination of calorimetric, total neutron scattering, PDF analysis and ab initio simulations resulted in an in-depth understanding of the disordering of pyrochlore to defect fluorite – a key property driving the stability of pyrochlore-type waste forms. Short-range ordering via weberite-type domains was identified in the disordered phases. A series of macroscopic and microscopic dissolution studies led to a comprehensive understanding of the dissolution behavior of these ceramics under repository relevant conditions and the rate controlling mechanisms.

Keywords: Nuclear waste management, Spent nuclear fuel, Ceramic waste forms

ABS 777

NANOSTRUCTURED OXIDE THIN FILMS FOR ENERGY HARVESTING

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Thin films of oxide materials are used in a wide range of sustainable energy-harvesting devices such as photovoltaics, photo(electro)catalysis and piezoelectric energy harvesters. Enhancement in all of these areas has been achieved through the use of nanostructured films, including nanorods/wires, nano/meso-porous films as well as many other structures. Such nanostructuring can give advantages particularly through the increase of interfacial area in the device where important processes such as charge transfer or reactions take place, as well as imparting improved mechanical properties. This talk will give an overview of some of our work using such nanostructured oxide films, from their synthesis using solution-based techniques, to applications including piezoelectric energy harvesting and photoelectrocatalysis. In particular, it will focus on the synthesis of materials that contain controllable electrical polarisation, such as piezoelectrics and ferroelectrics, e.g. ZnO, BaTiO3 and BiFeO3, and how these can be used to give enhanced properties in energy harvesting devices. First, our work on ZnO-based piezoelectric nanogenerators will be presented, in particular focussing on the motivation and benefits for the novel use of semiconducting polymer layers in these devices. Then the use of nanostructured ferroelectrics for photo(electro)catalysis will be presented, including ferroelectric-photocatalyst ‘nanocomposites’, e.g. BaTiO3-Fe2O3, through which we have demonstrated enhanced catalytic performance for solar water splitting compared to the isolated components.

Keywords: Nanostructured thin film, Piezoelectric, Photocatalysis

ABS 726

CONSTITUENT DEVELOPMENT FOR HIGHER-TEMPERATURE CAPABLE CERAMIC MATRIX COMPOSITES

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Two of the highest capability priorities for the Air Force, energy-efficient turbine engines and long-range precision strike require high-temperature ceramic-matrix composites (CMCs) to enable increased turbine engine efficiency and thermal protection of aero-structures. While the use of CMCs for these applications is desirable because of their low density, high strength, toughness and oxidation resistance, above all it is required due to their higher temperature capability compared with nickel-based superalloys. In the case of next generation turbine engines, both commercial and military, and for both air- and land-based applications, CMCs are being considered for structural components in the combustor and turbine sections, as well as throughout the exhaust section. For components in the hottest sections of future military engines, SiC/SiC CMCs currently lack the temperature capability and durability required to achieve performance goals and long life. The same holds for future applications in propulsion and commercial energy generation.

The most pervasive lifetime and temperature limitations for SiC/SiC CMCs are related to oxidation, creep and stress rupture of the fibers, oxidation-induced instability of the fiber-matrix interface, and instability of the matrix at temperatures >1400°C. Consequently, we are addressing these shortcomings by developing technology to enable higher-temperature capable SiC fiber, oxidation-resistant fiber-matrix interfaces, and improvements in processing of refractory matrices for turbine engine applications. This presentation highlights research that is addressing the need for improved high-temperature-capable SiC/SiC CMCs, with a focus on CMC constituents and an understanding of their processing, microstructure, and behavior in relevant service environments. The focus of this presentation will be on recent work in the area of oxidation-resistant fiber coatings and processing and characterization of PIP and a novel route to CVI matrices for SiC/SiC CMCs.

Keywords: CMCs

ABS 660

DIFFUSION-DRIVEN NANOSCALED TRANSFORMATIONS IN OXYGEN DEFECTIVE CERIUM OXIDE AND COMPOSITES

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Oxygen defective metal oxides are electric charge-carriers ceramics that are rapidly defining a new generation of ionic-electronic systems, for energy, electro-mechanics, sensing and advanced electronics. In energy technologies, they are especially emerging for their wide range of functions and tunability that are generally achieved at the nanoscale, where the materials are fabricated as nanoparticles by chemical strategies and as thin films by physical and chemical vapor deposition. Nanoscaled functional oxides have especially received great attention for the possibility to extend the interfaces. These have very different properties from the bulk and can play an important role in energy technologies.

However, large interfaces and nanoscales can also result unstable and unreliable, especially in high temperatures energy technologies, such as solid oxide electrochemical cell, high temperatures hydrolysis reactors, gas transport and separation technologies. Mass diffusion effects can progressively degrade performances of active components, leading to chemical contamination and even morphological modification. In this presentation, I show that elemental diffusion can be the key in controlling the final structure to the desired microstructure and in nano assembling, even under intense diffusive conditions. This is especially shown for a relevant case study, highly defective cerium oxide, a multi-functional key material in use in several energy technologies as dense, porous and in composites. Among some examples, I will show that by controlling defects and elemental diffusion novel pearlite-like heterostructures can be assembled via designed thermo-chemical processes, where oxygen defects are activated to trigger phases´ equilibria and rapid mass diffusion effects.

Keywords: cerium oxide, solid state diffusion, nanocomposites

ABS 642

EXPLOITING INTERFACES TO ENHANCE THE PERFORMANCE OF OXIDE THERMOELECTRICS

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In the last 15 years there has been growing interest in oxide thermoelectrics as alternatives to traditional metallic thermoelectrics which depend on rare, expensive, and sometimes toxic elements. The oxides are stable at high temperatures and generally lighter in weight and cheaper, and based on environmentally friendly materials. Many are based on perovskite structures and layer structures. A current limitation of oxides is the modest thermoelectric figure of merit (ZT), around 0.3 to 0.4, which comes from the low electrical conductivity and high thermal conductivity. In order to improve the material performance (by maximizing ZT) efforts have focussed on reducing thermal conductivity and electrical resistivity. One strategy is to employ microstructural engineering at the nanoscale to increase phonon scattering in order to reduce thermal conductivity. By taking examples from systems based on CaMnO3, (La,Sr)TiO3, ZnO and materials exhibiting self-assembly nanostructures, the nature and benefits of interface structures and precipitates will be examined. Details of atom level structures revealed by use of high resolution TEM and information from DFT modelling can reveal important mechanisms. Finally, the potential benefits of oxide-carbon interactions will be outlined.

Keywords: Thermoelectric, Oxide, Interface

ABS 499

PROTONICS IN PEROVSKITE MATERIALS FOR PROTONIC CERAMIC FUEL CELLS

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For the efficient operation of protonic ceramic fuel cells (PCFCs), the cathode materials require highly electrochemical activities not only for oxygen ions and electrons but also for protons (termed triple conducting oxides, TCOs). Although extensive efforts thus have been devoted to developing the TCOs, however, systematic development of the TCOs are limited due to the characterization challenges of protonic behavior in the TCOs. Herein, we comprehensively identified both thermodynamic and kinetic properties of proton transfer for the perovskite-type TCOs, including hydrogen tracer diffusion coefficient (D*H), surface exchange coefficients (k*H), and protonation enthalpy. Quantification of these properties is crucial to understanding the electrochemical behavior of TCO and the mechanistic details of electrode reactions, providing important insight into the knowledge-based design of more efficient electrode materials for high-performance PCFCs.

Keywords: Proton conducting oxides, Protonic ceramics fuel cells, Perovskites

ABS 462

PERFORMANCE OF CERAMIC MATERIALS FOR FUEL CELL AND CO-ELECTROLYSIS OPERATION OF SOLID OXIDE CELLS

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The electrodes for solid oxide cells (SOCs) have been optimized for operation in fuel cell mode (SOFC) during last decades. Several successful material combinations has been found and applied in cell manufacturing. The overview of reported data of investigated electrode materials provides guideline for operation limits and challenges to achieve an appropriate durability in stack and system environment. Similar material combinations has been initially used for operation in electrolysis mode (SOEC) and shown some drawbacks. The efficient high temperature electrolysis is nowadays of high interest for potential application in a renewable energy system. The possibility to use high temperature heat for the electrolysis reaction makes the SOEC technology an attractive option for the integration in process concepts for the production of valuable chemicals from renewable energies. Moreover, the SOEC allows for the electrolysis of water and carbon dioxide in a so-called co-electrolysis. While the co-electrolysis is more complicated than steam electrolysis, the electrochemical performance of electrolyte supported cell (ESC) with LSMM'/ScSZ and Ni/GDC electrodes were investigated over a wide range of operating conditions (SOEC as well as SOFC), varying the ratio of H2O:H2 and CO2:CO, the operating temperature (750–850°C) and current density. The fuel and air electrodes were modified for long term stable SOFC and SOEC operation. Improved cell was successfully tested for ~2400 hours at 803°C under co-electrolysis conditions (H2/H2O/CO2/CO mixture as fuel, j = -400 mA/cm2). The performance of ESC is compared with the state of the art of SOEC anode supported cells and challenges of future development will be discussed.

Keywords: solid oxide cell, fuel ad steam electrode, air electrode

ABS 965

ADVANCED INTERMEDIATE TEMPERATURE Na-METAL HALIDE BATTERIES FOR STATIONARY ENERGY STORAGE SYSTEM APPLICATIONS

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Recently, energy storage systems (ESS) consisting of large-scale rechargeable batteries are considered as one of the most important technologies to effectively integrate intermittent renewable sources , such as wind and solar, have variable output. Because there is less restriction on the energy footprint for ESS than portable devices, vast majority of battery technologies face great opportunities from cost perspective and technical horizon for ESS application. In particular, the use of a naturally abundant element, sodium (Na), as the charge carrier rather than lithium (Li) is an attractive way to reduce materials cost.

Over the past years, our team in PNNL has been focusing on studying intermediate temperature Na-metal halide (Na-MH) batteries, which present several advantages including simple cell architectures, improved thermal management, lower operating temperature, and lower manufacturing cost over high temperature Na based batteries. Material degradation in Na-MH batteries (particle growths) is significantly suppressed at lower operating temperatures (<200°C), which allow a prolonged cycle life and stable cell performances. We also put efforts to develop low cost cathode materials aiming the practical applications. In here, fundamental understandings of degradation mechanisms, materials development, and long-term cycling results for Na-MH batteries will be presented.

Keywords: Energy Storage, Na-metal halide battery, Intermediate temperature

ABS 210

KEY ISSUES IN THE MANUFACTURING OF PROTON CONDUCTIVE MULTILAYERS CERAMICS

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Zirconate and Cerate perovskites have recently received renewed interest as high temperature proton conductors for hydrogen separation and as electrolytes in solid-oxide fuel cells and/or electrolysers (SOFCs/SOECs).
The widespread application of these materials however is hindered by the need of high densification temperature and change in stoichiometry induced by the evaporation of some of the constituent.
This work will highlight and examine the main issues related to the production of planar defect-free multilayers with retained stoichiometry.
In particular, the importance of a proper lamination step and a suitable sintering atmosphere will be deeply considered and analyzed.
The results will clearly show as an high performance device can be obtained only if each single step of the production path (from the nature of the powder up to the sintering) is carefully considered and optimized.

Keywords: proton conduction, perovskite, high temperature cells

S06

CERAMICS FOR ENERGY CONVERSION AND STORAGE

ORAL PRESENTATIONS

ABS 855

IMPRESSION CREEP BEHAVIOR OF $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$

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Lanthanum strontium cobalt ferrite perovskite oxides with the general formula La1-xSrxCoyFe1-yO3-d (LSCF) have been extensively investigated as cathodes for SOFCs owing to their high ionic and electronic conductivity, as well as their good catalytic activity toward oxygen reduction. Recent studies on the mechanical behavior of such perovskites have reported their anomalous ferroelastic behavior in which the material exhibits a nonlinear behavior and hysteresis in strain-stress curve; and ferroelastic creep due to domain switching. Ferroelastic mechanical characteristics have been evaluated by compression and indentation techniques.

Indentation test using a cylindrical indenter with a flat-end known as impression test is a common technique for the mechanical characterization of materials, which has significant advantages over conventional compression test including small specimen volume similar to other indentation tests. Moreover, impression test gives a constant stress at constant load and simplifies theoretical analysis as the contact area is assumed to be constant throughout the loading period. Creep behavior of the material is characterized by recording the indenter displacement as a function of time at constant loads and equivalent strain rate can be evaluated from the impression velocity. For high-temperature creep, the creep strain can simply be described by a power law and for the ferroelastic creep as the number of switchable domains is limited, a Prony series-type equation with relaxation time would be more suitable.

The current study attempts to investigate impression creep behavior of a commercial LSCF by impression technique utilizing 2 mm diameter high alumina cylindrical flat-end punch. The calcined powder was then uniaxially pressed (120 MPa) to form green discs (D=12mm and t=3 mm) and which were subsequently sintered at 1200 °C for 3 h. The surfaces of sintered discs were grinded, mirror polished and paralleled by a modified diamond saw and annealed at 1000 °C for one hour. Heating and cooling rate for sintering and annealing are maintained at 60 °C/h and 30 °C/h, respectively. A universal material testing machine (Zwick/Roell) with one kN load cell is used for applying impression loads at different temperatures. The load is raised from 5 N to a load between 200 and 400 N held up to 3 h and unloaded to 5 N with loading and unloading rate of 120 N/min.

Keywords: Ferroelasticity, LSCF, Impression creep

ABS 354

STRUCTURAL, ELECTRICAL AND THERMAL PERFORMANCE OF THERMOELECTRIC Bi(RE)-Te CONTROLLED BY SYNERGISTIC CARRIER SCATTERINGS

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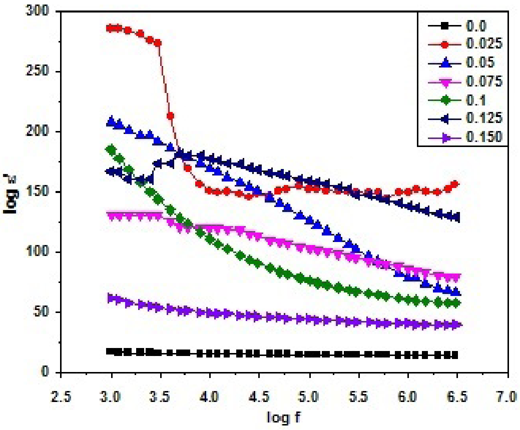
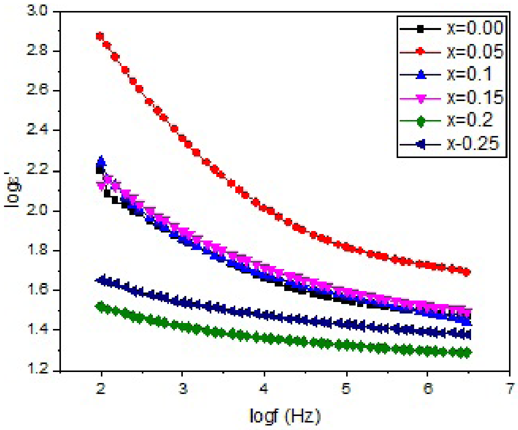
Thermoelectricity is a useful technology for recovering waste heat into electricity without pollution. Rare Earth doped bismuth telluride Bi2-xRExTe3 (RE = Gd, Nd; x = 0.00 - 0.25) were synthesized by a simplified method known as without water and surfactant (WOWs) sol gel method. X-ray diffraction technique was used for structural analysis of the samples. The analysis confirmed the single phase i.e. rhombohedral structure of as prepared and sintered samples. Fourier Transform Infrared Spectroscopy also showed phase purity of the prepared samples. AC electrical analysis was done as a function of frequency. The dielectric constant, dielectric loss and impedance showed decreasing trend while AC conductivity showed increasing trend with increase in frequency. At room temperature, composition Bi1.95Nd0.05Te3 and Bi0.025Gd1.975Te3 showed the best dielectric response. Therefore, these compositions are suitable candidates for energy storage devices, i.e. capacitors in microelectronic applications. The dc conductivity as a function of temperature was determined. The samples Bi1.95Nd0.05Te3 and Bi1.85Gd0.150Te3 with showed higher conductivity among other samples. I-V measurements showed semiconductor behavior of the samples. Advantageous transient plane source method (ATPS) was used for thermal transport properties i.e. thermal conductivity, thermal diffusivity and volumetric heat capacity. Thermal conductivity and volumetric heat capacity showed an increasing trend with temperature while thermal diffusivity decrease with increase in temperature. The thermal conductivity of sample Bi1.75Nd0.25Te3 and Bi1.85Gd0.150Te3 was lower than that of other samples. The samples with composition Bi1.75Nd0.25Te3 and Bi1.85Gd0.150Te3 are suitable for thermoelectric applications. Controlled synergistic carrier scatterings are very useful for suitability of these materials in multiple applications.

Keywords: Tellurides, Structure, Thermophysical



Dielectric constant of $Bi_{2-x}Gd_xTe_3$ (x= 0.0, 0.025, 0.05, 0.075, 0.1, 0.125 and 0.150) in the frequency range of 1 kHz to 3 MHz at room temperature.



Dielectric constant of $Bi_{2-x}Nd_xTe_3$ (x= 0.00, 0.05, 0.1, 0.15, 0.2, 0.25)

ABS 838

ENHANCED LOW-TEMPERATURE PROTON CONDUCTIVITY IN SULFUR-DOPED, BULK NANOSTRUCTURED OXIDES

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Bulk nanostructured simple oxides, such as TiO2, ZrO2 and CeO2, obtained by fast sintering of nanopowders have been shown recently to present a significant proton conductivity in the presence of humidity. It has been clarified that this conductivity is due to the transport of protons on the internal surfaces of the open nanopores present in these materials. These results are particularly interesting as simple oxides would be an interesting alternative to polymeric protonic conductors for low temperature applications due to their high chemical and mechanical stability, low toxicity, high melting point and low cost. However, in order to become a viable alternative to polymers the conductivity of these ceramics must be comparable or even higher.

We have shown recently that nanostructured titanium oxide, in form of anatase, shows a significant enhancement in the proton conductivity when doped with sulfur. The conduction properties of S-doped TiO2 have been thoroughly investigated in this work. Nanopowder of TiO2 have been synthetized through hydrolysis of titanium tetra-isopropoxide (TTIP) in water. S-doped nanopowders have been obtained in a similar way adding thiourea and H2SO4 to the solution as sulfur sources. Another type of sulfur doping has been obtained treating sintered samples in H2SO4 at different concentrations for 1 hour. A commercial anatase nanopowder containing a small amount of sulfur was characterized as well. The nanopowders have been sintered with high-pressure field-assisted sintering (HP-FAST) technique using a temperature of 500°C and a pressure of 600 MPa. Compositional and microstructural analyses were carried out, along with impedance spectroscopy and thermogravimetric analysis. Conductivity characterization were performed by impedance spectroscopy at different temperatures and different relative humidity (RH) values.

A gain of five orders of magnitude in the low temperature proton conductivity of nanostructured anatase was observed as result of the doping with sulfur. The samples with the higher content of sulfur reach conductivity values of 0.1 S·cm-1, close to the ones reported for perfluorinated polymer-based protonic exchange membranes. The results evidenced also that the conduction process is not influenced by the microstructure, but depends solely on the sulfur content.

Keywords: Low-temperature proton conduct, nanostructured materials, Field assisted sintering

ABS 814

OXYGEN EXCHANGE KINETICS AND ELECTRONIC CONDUCTIVITY OF THE THIRD ORDER RUDDLESDEN-POPPER PHASE $Pr_4Ni_{2.7}Co_{0.3}O_{10}$

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Objective Praseodymium nickelate Ruddlesden-Popper phases have attracted considerable interest as mixed ionic electronic conducting alkaline-earth free SOFC/SOEC air-electrode materials. This structure family comprises Ruddlesden-Popper phases with different Pr/Ni ratios and allows for partial substitution of Ni by Co. Here, the third order Ruddlesden-Popper phase Pr4Ni2.7Co0.3O10 (PNCO43) is investigated in terms of phase stability and electronic conductivity. Surface oxygen exchange kinetics of PNCO43 was studied on well-defined PNCO43 thin-film microelectrodes.

Materials & Methods The presence of the third order Ruddlesden-Popper phase was confirmed by XRD and Rietveld analysis. A two-step sintering process was applied to achieve dense pellets suitable for electronic conductivity measurements. The electronic conductivity of PNCO43 was determined at 50 ≤ T/°C ≤ 800 in the oxygen partial pressure range of 1×10-3 ≤ pO2/bar ≤ 0.1. Dense thin-film microelectrodes of PNCO43 were prepared by pulsed laser deposition and photolithography on yttria-stabilised zirconia single crystal substrates and investigated with X-ray diffraction, scanning electron microscopy and scanning transmission electron microscopy (including energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy) as well as inductively coupled optical emission spectroscopy. Surface oxygen exchange properties, as well as individual resistive and capacitive processes, were investigated on microelectrodes with electrochemical impedance spectroscopy at 550 ≤ T/°C ≤ 850 and 1×10-3 ≤ pO2/bar ≤ 1.

Results For the phase-pure, dense PNCO43 a high electronic conductivity (e.g. σe=265 S cm-1 at 600°C and pO2 = 0.1 bar) was observed. A high surface exchange coefficient (e.g. kq =3.5×10-6 cm s-1 at 850°C and 2×10-1 bar pO2) was obtained from the microelectrode impedance spectra. The activation energies for kq were in the order of 2 eV, depending on pO2. kq exhibits a pO2 dependence of kq ~ (pO2)^m with the exponent m in the range of 0.6-0.7. Chemical surface exchange coefficients of oxygen (kω^δ and k(Cchem)^δ) estimated from the peak frequency and the chemical capacity are in good agreement and indicate fast surface oxygen exchange kinetics (e.g. k(Cchem)^δ=6×10-3 cm s-1 at 800°C, pO2 = 0.2 bar).

Conclusions The cobalt-doping in PNCO43 improves the sinter activity of the material and increases the electronic conductivity compared to the undoped compound Pr4Ni3O10. PNCO43 thin-films show fast oxygen surface exchange kinetics with low oxygen partial pressures dependencies. Based on these results, PNCO43 can be considered a promising alkaline earth-free material for SOFC and SOEC air electrodes operated at intermediate temperatures of 600°C-800°C.

Keywords: Ruddlesden-Popper phase, solid oxide fuel cell cathode, oxygen exchange kinetics

ABS 808

PREPARATION AND CHARACTERIZATION OF PROTON-CONDUCTING MATERIALS BASED ON LANTHANUM NIOBATES FOR HYDROGEN SEPARATION MEMBRANES

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Rare-earth niobates are a promising group of materials due to the complexity of their structure and properties which qualify them as candidates for a variety of applications. LaNbO4 has been studied as a perspective type of proton conductor even though its conductivity is somewhat low. Many attempts have been made to improve the conductivity by single- or multi-element doping. In general, good mechanical properties, high stability in H2O- and CO2-containing atmospheres and compatibility with transition metals (Cu, Ni, Cu-Ni alloys) and their oxides [1, 2] make these compounds attractive for design of nanocomposite hydrogen separation membranes.

In our work lanthanum niobates LaNbO4, La0.99Ca0.01NbO4, LaNb1-xMoxOx and LaNb3O9 were synthesized using a modified Pechini route and mechanochemistry by high-energy milling. Structural and transport properties of sintered niobates were characterized by X-ray, Raman and IR- spectroscopy and 93Nb-NMR nuclear magnetic resonance, SEM, TEM, thermogravimetry and conductivity measurements. Besides, hydrated niobates have been investigated by using 1H-NMR. Oxide-oxide (La0.99Ca0.01NbO4+LaNb3O9) and metal-oxide (Cu0.5Ni0.5+La0.99Ca0.01NbO4 and Cu0.5Ni0.5 + LaNb1-xMoxOx) nanocomposites were prepared by treating the mixture of either complex oxides calcined at 700ºC or oxide + Cu0.5Ni0.5 powders in weight ratio 35:65. 5 wt. % by their ultrasonic dispersion in isopropanol. The powders of nanocomposites were pressed into pellets (d = 13 mm) and sintered using conventional thermal sintering as well as hot pressing under 50 MPa at 1100 °C. All obtained nanocomposite materials were characterized using XRD, SEM, TEM, impedance spectroscopy, oxygen 16O/18O (with C18O2) isotope heteroexchange. A wide range of methods were used to examine hydrated niobates and nanocomposites in order to ascertain the nature of H+-containing species and to get understanding of the mechanism of proton transport. Typical proton conductivity values are ~10 5 S/cm at 550 °C. OH migration appears to be more favorable way of migration than H+ jumps between O2 . H2O desorption experiments revealed the working temperature range being 300 – 450 °C.

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Keywords: hydrogen separated membranes, lanthanum niobates, nanocomposites

ABS 775

CRYSTAL STRUCTURE AND OXYGEN NONSTOICHIOMETRY OF LOW- AND HIGH- TEMPERATURE MODIFICATIONS OF THE THIRD ORDER RUDDLESDEN-POPPER PHASE $Pr_4(Ni_{0.9}Co_{0.1})_3O_{10}$-$\delta$

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Objective Mixed ionic-electronic conductors from the Ruddlesden-Popper (RP) series An+1BnO3n+1 (n=1, 2, 3 etc.) are highly interesting materials for fundamental investigations. However, especially for the higher order RP-phases (n>1), few systematic investigations on crystal structure, defect chemistry, and mass and charge transport properties are available. In the present study, the compound Pr4(Ni0.9Co0.1)3O10-delta (PNCO43) is characterised by in-situ X-ray powder diffraction (XRD), in situ high-resolution scanning transmission electron microscopy (HR-STEM), differential scanning calorimetry (DSC), and thermogravimetry (TG).

Materials & Methods The crystal structure of the high- and low-temperature modifications of PNCO43 was investigated by in situ XRD and Rietveld refinement from room temperature to 900°C in air. The phase transformation kinetics was studied by in situ XRD at 750°C and in situ HR-STEM. Further information on the phase transformation temperature was acquired by DSC and TG. The oxygen nonstoichiometry of PNCO43 was determined as a function of temperature (300-800°C) in the oxygen partial pressure range of 1×10^-3 < pO2/bar < 1.

Results PNCO43 shows a reversible transformation from the low-temperature monoclinic (P21, tilted octahedra) to the high-temperature tetragonal (I4/mmm, untilted octahedra) modification at 650°C in air. The related volume change is small (2%), and thus not expected to be detrimental for mechanical integrity. The phase transformation temperature as determined by DSC and TG agrees well with in situ XRD data. The oxygen nonstoichiometry of PNCO43 is in the range of 0.09-0.11 at 300 < T/°C < 800 and 1×10^-3 < pO2/bar < 1. The thermodynamic factors of oxygen are 3000-7000 at 300 < T/°C < 800.

Conclusions In the present work, new results on the crystal structure, phase transformation, and oxygen nonstoichiometry of PNCO43 were obtained. The oxygen exchange kinetics and the electronic conductivity of PNCO43 were investigated in a separate study [1]. Based on the results it can be concluded that PNCO43 shows interesting properties for potential applications in future energy technologies such as solid oxide fuel cell or solid oxide electrolyser cell air electrodes, electrochemical sensors, or oxygen exchange membranes.

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Keywords: Ruddlesden-Popper phase, Crystal structure, Oxygen nonstoichiometry

ABS 768

SOLID OXIDE FUEL CELL COMPONENTS BASED ON YTTRIA DOPED BISMUTH OXIDE

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Bismuth oxide exhibits extremely high oxygen ion conductivity and is recently discovered to have catalytic activity for oxygen reduction reaction, rendering this material very attractive for solid oxide fuel cell (SOFC) electrolyte and cathode applications. To stabilize the high conductivity cubic fluorite phase at the desired operating temperature range of 550-650 °C, bismuth oxide is usually doped with rare – earth oxides, such as; Y2O3, Er2O3 and etc.

In this study, fabrication of high performance electrolytes and cathodes based on yttria doped bismuth oxide is presented. Our experiments show that the temperature at which yttria doped bismuth oxide (YDB) is sintered to fabricate dense electrolyte ceramics has a significant effect on its phase and consequently, electrical conductivity stability. For example, sintering YDB at 800 °C results in a fast, exponential type of conductivity decay, accompanied by a phase transformation from cubic to rhombohedral. On the other hand, YDB ceramics sintered at 900-1100 °C results in a much slower, linear type of conductivity decay, showing no signs of phase transformation. The origin of this effect is explained by the premise that different sintering temperatures yield different amounts of metastable cubic phase, which is easily transformable to the lower conductivity rhombohedral phase.

For cathode applications, we use YDB in the form of a composite with lanthanum strontium manganese oxide (LSM) – the most widely used oxygen reduction electrocatalyst. The fabrication of this composite has been carried out by the spin-on deposition of a mixture of polymeric YDB and LSM precursors onto dense YDB electrolytes. This way, molecular level mixing of constituent cations is ensured, and the necessity of high temperature sintering is avoided. The resultant composite cathode structure is amorphous or crystalline, depending on the heat treatment temperature. Electrochemical impedance spectroscopy (EIS) analyses reveal that among the LSM-YDB thin film cathodes, the one that had not been heat treated prior to EIS measurements, i.e., the one that has an amorphous structure, exhibits the lowest cathode polarization resistance (e.g., 0.6 ohm.cm2 at 600 °C) and the highest stability.

Keywords: Yttria doped bismuth oxide, Electrolyte,Cathode

ABS 756

INTERFACE SOLID-STATE REACTIONS INVESTIGATED BY X-RAY MICROSPECTROSCOPY USING SYNCHROTRON RADIATION: ELECTRODE-ELECTROLYTE COUPLES FOR SOLID OXIDE FUEL CELLS

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The structural and chemical compatibility between electrodes and electrolytes for use in Solid Oxide Fuel Cells (SOFCs) is a critical issue: the materials should display similar thermal expansion coefficients, and most importantly the interdiffusion of chemical species at the interface has to be minimised. Chemical compatibility is commonly investigated by means of X-ray diffraction on powder mixtures and/or scanning electron microscopy/energy-dispersive spectroscopy on cross-sections of the bilayer assembly after prolonged annealing at high temperatures, to simulate both the long-term operation of a fuel cell and the thermal treatments necessary for processing.

This work reports on the application of X-ray microspectroscopy to evaluate the chemical and local structural fate of cations interdiffusing across several electrolyte/cathode bilayers. X-ray microspectroscopy combines an X-ray microprobe providing information on the spatial distribution of cations (X-ray fluorescence (XRF) maps) with chemical and structural information about the environment of atomic species, i.e. chemical and coordination state of cations, using space-resolved micro-X-ray absorption near-edge structure (microXANES). The interfaces were studied using the focused submicrometre-sized beam available at the SXM-II endstation on the ID21 beamline of ESRF.

Different electrode-electrolyte couples, annealed at 1150 C for either 12 h or 72 h, were analysed with this technique. Both proton conductors such as BaCe0.9Y0.1O3 (BCY) and La0.98Ca0.02NbO4 (LNC), [1] and an oxide-ion conductor, Ce0.8Sm0.2O2 (SDC), [2] were studied in combination with common cathode materials. The effect of prolonged thermal treatment on cation diffusion, accumulation of cations at the interface and the eventual formation of secondary phases in some of the bilayers will be shown.

The present results represent the first application of X-ray absorption spectroscopy to the study of materials compatibility for ceramics, specifically in materials for SOFCs. This approach can be extended to other materials or complete SOFCs: this can give insight on the mechanisms governing electrolyte-electrode compatibility and electrochemical performance in SOFCs.

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Acknowledgements
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Keywords: chemical compatibility, x-ray microspectroscopy,XANES

ABS 711

INNOVATIVE OXIDATION PROTECTIVE COATINGS FOR THERMOELECTRIC MATERIALS

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Higher manganese silicide (HMS), magnesium silicide and tetrahedrite (THD) are considered promising thermoelectric substrates to generate electricity from waste-heat recovery. A critical issue is the stability over time and the oxidation resistance at temperatures higher than 500°C for Mn- and Mg-silicides and above 350°C for THD, respectively. Glass-based materials, with low electrical and thermal conductivity, are potentially good candidates as protective coating materials for silicides- based thermoelectrics.

In this work a HMS substrate (MnSi1. 74), densified by spark plasma sintering (SPS), was coated with a silica-based glass-ceramic material. As sintered and glass-ceramic coated HMS samples were subjected to thermal cycling from room temperature to 600°C in air. The oxidation of the uncoated HMS led to the formation of a Si-deficient layer (MnSi) and a silica scale, resulting in a higher electrical resistivity and a reduced power factor. The coated samples showed electrical resistivity, power factor and zT comparable to the as sintered sample, thus demonstrating that the use of a glass-ceramic coating is an efficient oxidation protective system during cyclic working conditions. The self-healing property of the glass-ceramic coating at T > softening temperature was also demonstrated, thus confirming its ability as cracks sealant to enhance the reliability and durability of the coated thermoelectric system.

Moreover, a new silica-based glass-ceramic coating for Sn- and Sb- doped magnesium silicide (Mg2Si0.487Sn0.55Sb0.13) was designed in order to improve the long-term reliability of the thermoelectric module and its efficiency.

Since glass-ceramics would require a too high deposition temperature for tetrahedrite, the potential effectiveness of a commercial hybrid coating (ceramic-polymer) with low temperature curing was evaluated. The morphological, structural and thermoelectrical properties of the zinc- doped tetrahedrite (Cu11.5Zn0.5Sb4S13), densified with SPS, were reviewed, comparing the results obtained after a preliminary ageing in air (from room temperature to 350°C), with and without the coating. The hybrid coating resulted to be effective at providing an oxidation barrier coating and it is a promising candidate for protecting THD against high temperature oxidation in air.

Keywords: Glass-ceramic, Coating, Oxidation

ABS 692

TORSION TEST OF JOINED SOLID OXIDE FUEL CELL COMPONENTS AT ROOM AND HIGH TEMPERATURE

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Solid Oxide Fuel Cells (SOFCs) are devices able to convert chemical energy into electrical energy by red-ox reactions between a fuel and an oxidant. In order to obtain a satisfying output power it is necessary to build a SOFC stack. Some of the stack elements (i.e. metallic interconnect and ceramic cell) are joined by a sealant. The sealing materials should show high gas tightness, thermo-chemical and thermo-mechanical compatibility with the coupled materials, as well as mechanical stability in the relevant operating conditions. The most widely used sealing materials have up to now been based on glass-ceramics. For this reason, the mechanical strength of SOFC joined parts (interconnect/cell) is an important information for design and prediction of their behaviour at room temperature and in working conditions. To evaluate the shear strength of joined components, currently most of the test methods are based on lap-shear configurations. These tests are useful for comparison purposes, but unsuitable to provide pure shear strength for design and modelling purposes.

In this study the shear strength, of glass-ceramic joined steel samples, was evaluated with torsion test at room and working temperature (800°C).

The interconnect steel is Crofer22APU and the tested joining materials are glass-ceramic sealants with typical compositions based on silica containing BaO as modifiers.

Hourglass shaped samples were joined and then tested in torsion, confirming the suitability of this test to measure the shear strength of joined components. The results for samples with different joined area were compared, as well as results between sample tested at room and high temperature (up to 800°C). Also the Elastic and elasto-plastic behavior of the sealants at the different testing temperatures were compared.

Fracture surfaces after torsion test were analyzed with Scanning Electron Microscope equipped with EDS to evaluate the adhesive, cohesive or mixed failure behavior to understand the measured results.

Keywords: Joining, Torsion, Sealants

ABS 686

MICROSTRUCTURE AND ELECTROCHEMICAL PERFORMANCE OF POLYMERIC PRECURSOR DERIVED $La_{1-x}Sr_xFeO_3$ THIN FILM CATHODES FOR SOLID OXIDE FUEL CELLS

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Many materials with perovskite structure are used as a cathode material in solid oxide fuel cells (SOFCs) due to their high catalytic activity, electronic and ionic conductivity properties. Mostly, SOFC cathodes are produced by sintering a mixture of perovskite and ionic conductor electrolyte materials at high temperatures (e.g., 1100-1250 °C). This leads to large cathode particle size and poor performance. Also, it may cause formation of undesired phases (e.g., La2Zr2O7) at the perovskite/ionic conductor interface. La1-xSrxFeO3 (LSF) is a promising material for SOFC cathodes because i) it is a mixed ionic-electronic conductor (MIEC) with high electrocatalytic activity and ii) it does not contain environmentally hazardous elements, such as Co.

Single phase LSF or LSF-YSZ composite cathode materials produced by conventional sintering or infiltration methods using aqueous nitrate solutions exhibit high polarization resistance. In this study, it is aimed to produce single phase LSF thin film cathodes using polymeric precursor deposition method, which does not require high sintering temperature and is cost-effective. This way, i) achievement of small particle size and ii) prevention of undesirable reactions due to high temperature processing is proposed.

X-ray diffraction analysis (XRD) were performed on LSF gels obtained by drying the polymeric precursors and calcining at 700-900 °C. Pure rhombohedral La0.6Sr0.4FeO3 (LSF) phase was obtained in the case of calcination at 700 °C for 3 hours. The microstructural analysis of the LSF cathodes formed on YSZ substrate by the spin-deposition of the polymeric precursor solution process by scanning electron microscopy showed that the smallest particle size with a porous structure was obtained at 700 °C for 3 hours. Electrochemical impedance spectroscopy (EIS) measurements performed on symmetrical half-cells in the LSF/YSZ/LSF form revealed that ohmic resistances matching the resistivity of the YSZ and cathode polarization resistances as low as 0.5 ohm.cm2 at 700 °C was obtained.

Keywords: polarization resistance, cathode, impedance

ABS 683

UNDERSTANDING THE OXYGEN TRANSPORT MECHANISMS THROUGH A MIXED-CONDUCTOR MEMBRANE

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The oxygen transport membrane is of great interest for the development of new oxygen production units at low energy cost and low environmental impact. The technology of oxygen transport membrane is based on the mixed electronic and ionic conduction through the membrane material. However, the membrane material requires also a judicious compromise between the electrochemical performances, chemical stability and mechanical performances under operating conditions. Unfortunately, the oxygen transport mechanisms through the membrane are not well understood, and the formalism associated to these oxygen transport mechanisms, in particular at the membrane surfaces, shows some discrepancy with the experimental data given in the literature.

In this context, this talk will focus on recent progress about the better understanding of oxygen transport mechanisms through the membrane. An original setup based on the oxygen semi-permeation method to evaluate the electrochemical properties of the mixed conductor membrane (that are, the oxygen diffusion coefficient, Do, and the surface exchange coefficients, ki and kd) close to the working conditions will be presented, Figure 1 [1,2].

A particular attention is given to the understanding of oxygen transport mechanisms through one of the most promising materials presented in the literature, i.e. BaxSr1-xFeO3-δ perovskite series.

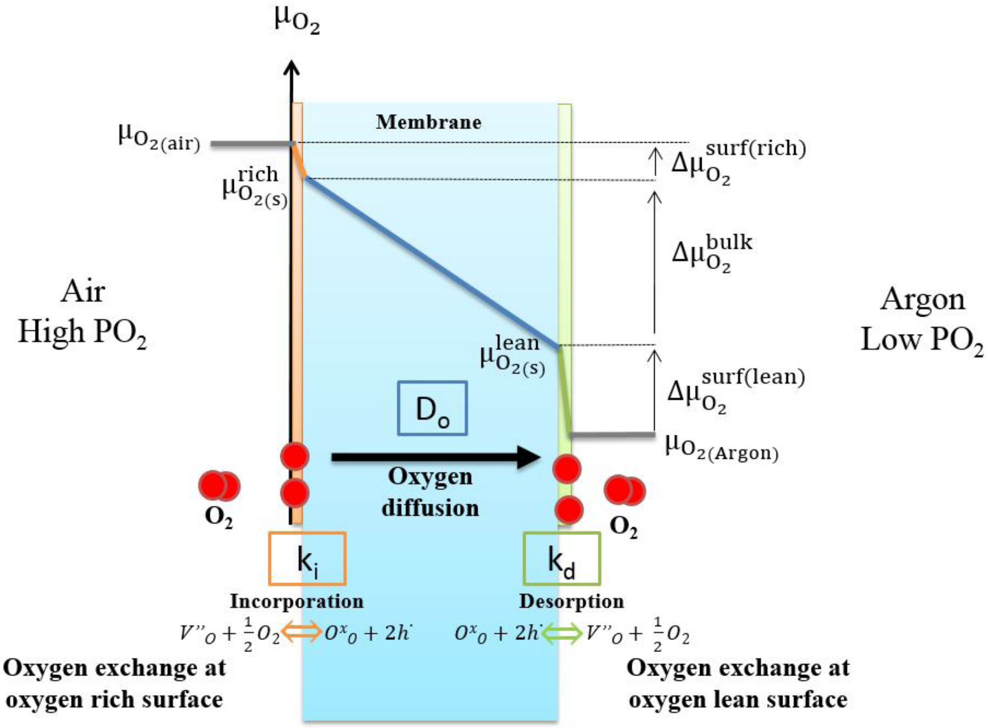

Figure 1: Profile of oxygen chemical potential through BaxSr1-xFeO3-δ membrane obtained at 900°C under air/argon gradient from oxygen activity measurements on oxygen rich and oxygen lean surfaces

Keywords: oxygen diffusion, oxygen surface exchange, mixed conductor

ABS 666

CRYSTALLIZATION, MICROSTRUCTURE AND ELECTROCHEMICAL PERFORMANCE OF $La_{0.8}A_{0.2}MnO_3$ (A:Sr, Ca)-$Ce_{0.8}Sm_{0.2}O_2$ THIN FILM CATHODES FOR SOLID OXIDE FUEL CELLS

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Energy conversion with solid oxide fuel cells (SOFCs) relies on the electrochemical reactions that take place at the junction of the electrocatalyst, ionic conductor, and gas phases (that is, the triple-phase boundary, TPB) in their electrodes. The performance of SOFCs depends on the rate of electrochemical reactions that take place at TPBs. At high SOFC operation temperatures (800-1000°C), shortening of TPB lengths caused by microstructural coarsening is observed, and is consistent with a drop in the electrode performance. To compensate for the degradation in electrode performance caused by slower electrode reaction kinetics, we propose developing electrode materials with long TPB lengths by a new method based on polymeric precursors.

To obtain long TPBs in electrodes composite electrode materials are typically fabricated by solid-state co-sintering of the electrocatalyst and ionic conductor materials in powder form at high temperatures (1100-1250°C). This approach results in electrode microstructures with relatively coarse particle sizes. In this study, to fabricate a composite cathode, we used the polymeric precursor method, which involves mixing polymeric electrocatalyst and ionic conductor precursors, both prepared by the chelation of cations constituting the desired phases in ethylene glycol. This method does not require high sintering temperatures and allows molecular level mixing of cations, resulting in the formation of a microstructure with small particle sizes and the consequent long TPBs in the cathode. For this study, we selected LaMnO3 doped with either Sr or Ca (LSM or LCM) as the electrocatalyst and Ce0.8Sm0.2O2 (SDC) as the ionic conductor.

The crystallization behavior of composite cathodes was investigated by x-ray diffraction (XRD), differential thermal analyses and transmission electron microscopy-energy dispersive x-ray spectroscopy (TEM-EDX) measurements. XRD studies revealed that the crystallization of both perovskite and ionic conductor phases are observed at around 700°C. On the other hand, the crystallization of the perovskite and ionic conductor phases from polymeric precursors was inhibited in the presence of the other phase. TEM-EDX analyses were in agreement with XRD results and revealed a microstructure with an average particle size of ca. 100 nm. Electrochemical impedance spectroscopy (EIS) measurements revealed that i) cathode polarization resistances below 2 ohm.cm2 can be obtained at 600°C and ii) cathode polarization resistance decreases significantly when both phases have crystallized.

Keywords: composite cathodes, triple phase boundaries, cathode resistance

ABS 652

TRIPLE-PHASE CERAMIC 2D NANOCOMPOSITE WITH ENHANCED THERMOELECTRIC POWER FACTOR AND ITS APPLICATION IN THERMOGENERATORS

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Sol-gel process was used to produce heavily doped misfit-layered cobaltate Ca3Co4O9 [1], which by subsequent heat treatment in suitable atmosphere self-assembled into 2D nanocomposite as confirmed by high-resolution transmission electron microscopy (HRTEM) [2,3]. Nanocomposite was preserved in sintered ceramic, which showed enhanced thermoelectric properties parallel to the cold-pressing direction as applied to the green . This went along with the preferential alignment of multiphase misfit-layered oxide platelets as confirmed by scanning electron microscopy (SEM). HRTEM confirmed 2D nanoslabs of three individual thermoelectric oxides, which contributed synergistically to the thermoelectric properties of the nanocomposite. By increases in both the isothermal electrical conductivity and the Seebeck coefficient, the power factor was enhanced to 6.5 µW cm-1 K-2 at 1073 K in air. According to Ioffe plots, i.e. thermoelectric power factor versus electrical conductivity, 2D nanocomposites where chosen to manufacture prototype thermogenerators (TEGs) [4]. The electric current-power characteristics of TEGs hint to the primary importance of the power factor compared to the thermoelectric figure-of-merit when a high electric power output is desired.

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Keywords: power factor,2D nanostructure, nanocomposite

ABS 641

ELECTRICAL ASSESSMENT OF $Ce_{0.1}Gd_{0.9}O_{1.95}$ WITH ADDED ALKALINE SALTS

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Ceria-based solid solutions are extensively studied as competitive substitutes of doped zirconia, the reference electrolyte used in Solid Oxide Fuel Cells (SOFC). Ceria-based ceramics, namely Ce0.1Gd0.9O1.95 (CGO), have high ionic conductivity. The main drawbacks of this material are the onset of electronic conductivity when exposed to reducing conditions, and the usually high firing temperatures (>1400 °C) needed to reach full densification of high purity powders. The use of sintering aids to lower the sintering temperature or the development of oxide+salt composites are alternative solutions to single phase pure ceria-based electrolytes. This work addresses the impact of sintering aids or significant levels of a salt (alkaline carbonates) on the electrical properties of CGO-based materials.

Pellets of Ce0.9Gd0.1O1.95 (CGO) with additions of (Li,Na)2CO3 (NLC) or (Li,Na,K)2CO3 (KNLC) (as minor sintering aid or substantial second phase) were fabricated using distinct processing routes (ceramic or chemical) and firing temperatures. The effects of these additions on the structure and microstructure were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Complementary, impedance spectroscopy measurements were performed between 200 and 750 °C in air or as a function of the oxygen partial pressure (pO2) down to about 10-20 atm.

XRD analysis indicated that the alkaline salts do not influence the cubic structure of CGO. Density measurement results showed that, with small additions of NLC, the densification could reach 96 % at 1100 °C. Electron microscopy revealed dense well-developed microstructures. The superior conductivity of composites with respect to pure CGO was confirmed above the distinct salt eutectic temperatures, reaching values in excess of 0.1 S/cm at 500 °C or even at lower temperatures. The analysis of electrical properties under variable pO2 conditions showed that minor salt additions had mostly a small impact on the n-type conductivity, when compared to pure CGO. This information is valuable in order to exploit alternative solutions in fuel cell development.

Acknowledgements
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Keywords: CGO, Sintering aid, Ionic/electronic conductivity

ABS 614

EFFECT ON THERMOELECTRIC PROPERTIES OF SUBSTITUTIONS ON THE BARIUM SITE IN THE NEW LAYERED COBALT OXIDE $Ba_2Co_9O_{14}$

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Objectives Recently, Delorme et al. [1] have shown promising thermoelectric properties in dense Ba2Co9O14 ceramics sintered by Spark Plasma Sintering. Cation substitution is a well-known method to tune the charge carriers density and the electrical properties as well as reducing the thermal conductivity [2]. Therefore, the objective of this work is to try to improve the thermoelectric properties of Ba2Co9O14 by substitution of barium by lanthanum, sodium or strontium.

Material and method (Ba1-xAx)2Co9O14 samples have been synthesized by solid state reaction and sintered by Spark Plasma Sintering Their electrical properties were measured by Ulvac ZEM-3 from 323 to 1000 K. Thermal conductivity is a product of density, thermal diffusivity, and specific heat capacity. Bulk density was determined from the dry mass and the geometric dimensions of pellets. Thermal diffusivity (Netzsch LFA457) was performed from 373 K to 1000 K in air and the data were average values of three measurements at each temperature. Specific heat capacity was measured from room temperature up to 1000 K, with a heating rate of 20 K.min-1 in platinum crucibles in a nitrogen atmosphere (Netzsch STA 449 F3 Jupiter)

Results The power factor at 1000 K (1.2 x 10-4 Wm-1K-2) is close to half of the value measured for Ca3Co4O9 (3 x 10-4 Wm-1K-2). The thermal conductivity is low, in the range 1.5 - 3.2 Wm-1K-1. However, at high temperature, it increases when temperature increases. At 1000 K, the thermal conductivity is 1.5 times Ca3Co4O9 one. Therefore, ZT value at 1000 K is 0.04, which is about one quarter to one third of the ZT value of Ca3Co4O9. Moreover, the ZT curve is relatively flat from 660 to 1000 K. A second measurement of the same sample has shown similar power factor values, emphasizing the stability of the compound even at high temperature in the low pressure He gas atmosphere of the ZEM-3.

Conclusion Substituted dense Ba2Co9O14 ceramics appears as promising p-type thermoelectric materials at high temperature for both applications and physics studies.

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Keywords: layered cobalt oxydes, Spark Plasma Sintering

ABS 608

FIRST PRINCIPLES ASSESSMENT OF CERAMIC-BASED THERMOELECTRIC AND THERMIONIC MATERIALS FOR DIRECT ENERGY CONVERSION

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Solid state power conversion devices, such as thermoelectrics and thermionics, depend solely upon the temperature gradients for their operation. In the case of thermionic conversion, the system performance is totally dictated by the thermal gradient and the work function of the electrode collector relative to the emitter electrode. Combined with a thermoelectric device, high efficiencies are possible. New materials must be developed that can meet the requirements to harvest waste enthalpy.

Computational methods offers an efficient and systematic manner to design new materials and guide there development. A computational -based material approach was used to determine the suitability of various materials as a practical thermoelectric and thermionic converters. The calculations were carried out using a projector augmented wave (PAW) method using a commercial code (Materials Design Inc.) MedeA incorporating the Vienna Ab-initio Simulation Package (VASP) as the computational engine. The calculation were based on density functional theory using the GGA-PBE exchange-correlation functional using and optimized mesh.

This study makes predictions and comparison between experimental and theoretical data of electrical, structural, and crystallographic properties. Comparisons are made between predicted and experimental measurements of Seebeck coefficients, thermionic emissions current and work function

Computational methods parameters can be used for predictions and to aid in the development of ceramic materials. Some descriptions (band structure) are very sensitive to such things as mesh density. Ceramics such oxide pyrochlores have potential as thermometric materials. Reasonable assessments and predictions can be made to determine thermionic materials properties for direct energy conversion.

Keywords: Thermoelectric, Thermionic, DFT Calculation

ABS 587

INVESTIGATING THE AGING EFFECTS OF FORSTERITE FOR SOLID OXIDE FUEL CELL APPLICATION

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Forsterite might be an attractive substrate material for Solid Oxid Fuel Cells (SOFC), due to its easy manufacturability, chemical stability, linear thermal expansion coefficient and low costs.[1] However, common operating temperatures of about 800 °C can cause changes in the phase composition and microstructure that might influence mechanical properties. Until today, not much is known about the effect of high temperatures on the characteristics of Forsterite. Therefore, in this study the behavior of forsterite under SOFC operating conditions was investigated with particular attention to the effect of temperature and humidity on the mechanical properties. For this purpose, the aging effect on the strength distribution, the hardness as well as the fracture toughness were investigated. To do so, thermal aging under ambient atmosphere as well as hydrothermal aging (e.g. autoclave) tests were performed. While thermal aging tests were performed at 750 and 950 °C for 10/ 30/ 90 days, autoclave aging was performed at 200 °C for 1/ 7/ 30 days. Beside the effect of aging, the fracture toughness KIC was investigated at various temperatures based on lamp irradiation method using edge notched circular disc [2], too. To determine the microstructural and chemical changes, all samples were characterized by using light microscope, scanning electron microscope (SEM) and X-ray diffraction techniques (XRD).

As a result, thermal aging leads to a slight increase of the hardness while autoclave aging results in a slight decrease compared to the unaged state. On the other hand, thermal aging as well as autoclave aging cause a slight decrease in fracture toughness. Double-ring bending tests reveal that characteristic strength slightly increases after thermal and autoclave aging.

Preliminary results of the fracture toughness determined via lamp irradiation method are in good agreement with the fracture toughness determined via Indentation Crack Length method (ICL) at RT. Experiments at higher temperatures indicate an increase of the fracture toughness with increasing temperature.

Beside the mechanical testing, XRD investigations show the presence of a secondary phase, which is also confirmed by SEM analysis.

In the presentation, correlations of the results will be deduced and the effect of different aging conditions will be evaluated. In addition, the effect of the secondary phases on the mechanical properties will be discussed critically.

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Keywords: Forsterite, Mechanical Properties, Aging

ABS 584

DEVELOPMENT OF A CHEMICALLY STABLE CARBONATE-CERAMIC MEMBRANE FOR CO_2 SEPARATION IN WATER-GAS-SHIFT REACTORS

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Synthesis gas with a CO/H2 ratio suitable for production of energy carriers, e.g. hydrogen, methanol, and gasoline, can be produced by gasification of solid fuels with subsequent water-gas-shift (WGS) reaction. The separation of CO2 using conventional absorption processes leads to high efficiency losses. In contrast, a membrane reactor containing a catalyst provides the opportunity for significantly reduced efficiency losses. The present work aims at developing a chemically stable membrane for separation of carbon dioxide in gasification atmosphere. The desired membrane consists of two phases, a porous ceramic oxygen ion conductor filled with molten carbonate. Both phases need to be stable under the relevant process conditions, i.e. syngas at up to 800 °C, and compatible with each other and the water gas shift catalyst. In a first step, potential oxygen ion conductor materials, e.g. cerium gadolinium oxide (CGO) and cerium samarium oxide (CSO), which are known from literature to be compatible with alkali carbonate melts, were exposed to different gasification-relevant gas atmospheres at 600-900°C and subsequently investigated regarding chemical reactions. In a second step, potential molten carbonate materials, e.g. Li2CO3/CaCO3 (eut.) and Li2CO3/SrCO3 (eut.), which are known from the investigation of phase diagrams and thermodynamic properties of alkali and alkaline earth carbonate systems, were investigated in differential thermal analyses on their melting and decomposition behavior. CGO and CSO have been sintered at different temperatures to obtain a suitable porosity. Furthermore, the wetting behavior between the molten carbonates and the ceramics (CGO and CSO) was investigated. Finally, dual phase materials consisting of the ceramics and the eutectic mixtures of the carbonates were annealed in contact with WGS catalysts under different gasification-relevant gas atmospheres at 600-900°C and subsequently investigated regarding chemical reactions.

Keywords: CO2 separation, Water-Gas-Shift-Reaction, Dual Phase Membrane

ABS 580

HYBRID ELECTROLYTES FOR ALL SOLID-STATE LITHIUM BATTERIES: DEVELOPMENT OF $Li_7La_3Zr_2O_{12}$ MATERIAL

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Currently, high energy lithium-ion batteries are the main portable power sources due to the growing use of electronic devices. Moreover, lithium batteries could play a much bigger role due to the growing sector of electric vehicles. However, current commercial lithium-ion batteries consist of organic electrolytes, which provide good battery performances but suffer from safety problems. This main issue could be addressed using solid-state electrolytes, such as polymer or inorganic lithium-ion conductors. This work focuses on a third kind of solid-state electrolyte called hybrid, where ceramic particles are dispersed in a polymer electrolyte matrix. This hybrid electrolyte could bring the advantages of both types of electrolytes: good interfaces, low cost and weight, and simple implementation for polymer and high conductivity, good mechanical strength, electrochemical stability and separator role for ceramic. The study concerns, more precisely, the impact of the ceramic filler based on a garnet material, Li6,25La3Zr2Al0,25O12 (LLZO). Compare to other materials of the state of the art, LLZO material has various advantages, such as high ionic conductivity (~1.10-3 S.cm-1), good chemical stability and wide electrochemical window.

Various hybrid electrolytes were made using a mixture of LLZO ceramic and a conductive polymer, with the addition of lithium salts (LiTFSI). Electrolytes performances were evaluated using impedance spectroscopy and electrochemical testing. LLZO ceramic material was made using different synthesis routes in order to control the morphology of particles. 3D ultraporous structures were also manufactured to improve LLZO percolation in the polymer, in order to develop a direct ceramic pathway for Li+ conduction. Surface modification of LLZO was assessed in order to see the possibility to improve the synergy between LLZO and the polymer at the interface.

During this study, LLZO powders were obtained with different morphologies and with shape factor between 1 and 100 (“potatoid”, needles, and wires). Hybrid electrolytes were successfully produced and optimized. Finally, the impact of parameters such as: polymer/ceramic ratio, morphology of LLZO particles, LLZO surface modification, and arrangement of Li+ conduction ceramic pathways, were investigated on hybrid electrolyte properties.

This work allows a better vision of hybrid electrolytes requirements in terms of conductive ceramic compound.

Keywords: Hybrid electrolytes, garnet - LLZO, synthesis / shaping processes

ABS 551

CLEANING WITH PHOTONS: NANOPOROUS, FLEXIBLE TITANIA FILTERS FOR SUSTAINABLE WATER STERILIZATION

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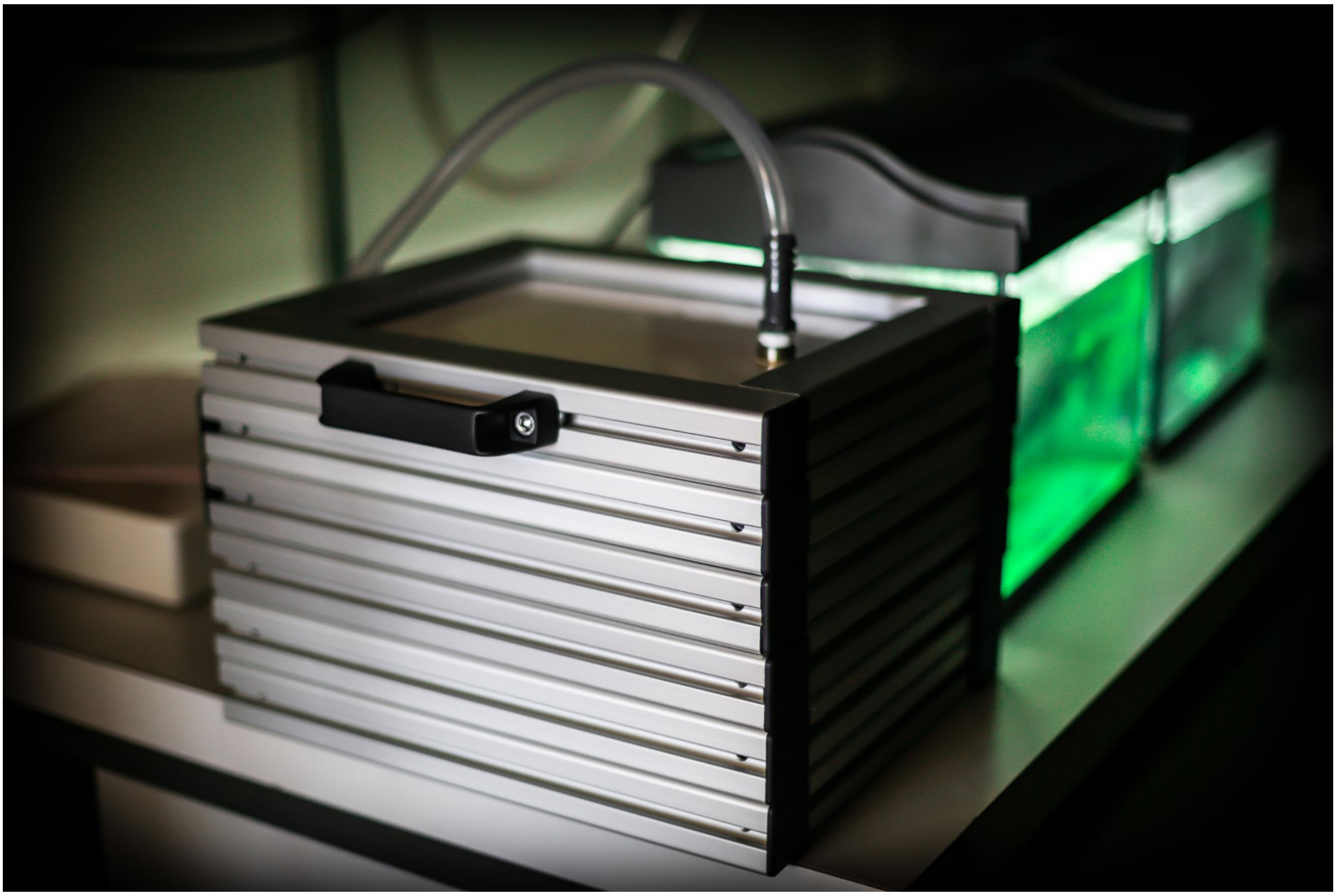
The discovery of photocatalytic water splitting and photocatalysis dates back to the 1970s. Since then, several semiconductor nanoparticles have been found to have remarkable photocatalytic activity to eliminate health-threatening bacteria, viruses, worms and persistent, bioaccumulative organic water pollutants as pharmaceuticals, pesticides and endocrine disruptors. Surprisingly, despite significant research efforts, studies have mainly remained in the stage of laboratory experiments and only a limited number of products using this technology can be found on the market. Materials and devices with sufficient efficiency, stability and low cost are yet to be demonstrated. Among the known semiconductor photocatalysts, titanium dioxide (TiO2) is the most popular owing to its excellent chemical stability, low toxicity and low cost.
I will discuss the performances of a low cost, durable and easy to operate solar-thermal water purification prototype device based on novel, nanoporous ceramic titania filters. Field test results confirm that these trough-flow, zero-power devices allow the production of bio-hazard-free drinking water from contaminated water resources.

We gratefully acknowledge the financial support of SARECO.

Keywords: nanowire, self-cleaning, flexible



ABS 544

POLYMER-DERIVED SiOC CERAMICS FOR ENERGY STORAGE APPLICATIONS

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Considering the relatively lower capacity and charge-discharge rate of currently commercial Li- ion batteries with graphite as anode material, lots of efforts have been employed to explore new anode materials to achieve the high performances, such as high energy density, large capacity and long life span. As promising candidates, Si-base anode materials have attracted a lot of attention because of their super-high theoretical Li-storage (an order of magnitude higher than for a graphite anode). However, the high volumetric change during the cycling of lithiation and delithiation and poor conductivity restrict their application in Li-ion batteries. In this work, we used as anode material polymer-derived SiOC containing conductive agents, to achieve low volumetric change and high structural stability. Additive manufacturing (direct ink writing) was used for the fabrication of regular, reproducible SiOC geometries, in the quest for 3D printing of all-component Li-ion batteries or super-capacitors with high performances, in the future.

Keywords: SiOC, anode material, additive manufacturing

ABS 513

INFLUENCE OF SEED LAYER MODIFICATION WITH RGO AND ANNEALING CONDITIONS OF ZnO NANOROD ARRAYS ON MORPHOLOGICAL AND PHOTOCATALYTIC PROPERTIES

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ZnO nanomaterials have been widely studied over the past decade due to their significant performance in technological applications such as optics, electronics, and photonics. In recent years, one dimensional (1D) ZnO nanorods have been used in photocatalytic applications, especially for the degradation of pollutant molecules dissolved in waste waters. In the present study, the effect of ZnO seed layer layer modification with reduced graphene oxide (rGO) and annealing temperature on the orientation of ZnO nanorod arrays grown on glass substrates with three stages were investigated. Graphene oxide synthesized by the Hummer's method was reduced chemically by hydrazine hydrate and rGO was obtained. The oxygenated functional groups of rGO have been supported the ZnO seed layer as by acting nucleation centers to grow ZnO nanorods. ZnO seed layers were successfully deposited on glass substrates by dip-coating method and annealed at 250, 350, 400 and 500C. Morphologies and structures of the samples were investigated by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD), respectively. The diameters of the nanorods are decreased with increasing temperature. The strong diffraction peak (002) in XRD patterns are revealed the preferential orientation along the c-axis. The photocatalytic degradation efficiency of all synthesized structures was determined by a selected pollutant dye under UVA radiation and it was observed that degradation rate was increased with modification of rGO.

Keywords: ZnO nanorods, rGO, photocatalytic

ABS 507

ENHANCING THE MECHANICAL PROPERTIES AND AGING STABILITY OF ZIRCONIA BASED SOLID OXIDE FUEL AND ELECTROLYSIS CELLS SUPPORTS

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High mechanical robustness is one of the main requirements for a reliable long-term use of solid oxide fuel and electrolysis cells. To further increase the cell size, and hence facilitate further development of the technology, special attention needs to be paid to enhancing the mechanical reliability of the cells.
We have investigated improving the mechanical properties of Ni(O)-stabilized zirconia SOFC/SOEC supports using two classes of zirconia materials: first, zirconia with transformable (metastable) tetragonal phase to achieve the tetragonal to monoclinic phase transformation toughening, and second, non-transformable (stable) tetragonal zirconia in which the ferroelastic toughening provides enhanced mechanical properties. In this presentation, the focus is on our results on the first class of stabilized zirconia materials. In transformable tetragonal zirconia based ceramics increasing the transformability of the tetragonal phase results in more efficient toughening, as the material can more readily undergo the energy dissipating tetragonal to monoclinic phase transformation. This can be achieved by reducing the amount of stabilizer. The results of this study showed that lowering the yttria content from 6 mol% YO1.5 (i.e. 3YSZ) to 5 mol% (i.e. 2.5YSZ) improved the mechanical properties of the zirconia based supports. However, it negatively influenced their high-temperature aging resistivity; as a large amount of monoclinic phase (~35%) was formed after aging at 800°C (the typical operating temperature of SOCs) within 850 h. To mitigate this, different supports made of zirconia co-doped with ceria and yttria (with effectively similar stabilizer contents) had superior resistivity to aging at high temperatures, and with a toughness enhancement over state-of-the-art 3YSZ based support (up to 30 % higher for 1.5 mol% CeO2 and 4.5 mol% Y2O3). Co-doping with Ceria and yttria is therefore a more promising approach to ensure both the high mechanical properties and aging resistivity.

Keywords: Ni(O)-Zirconia support, Mechanical properties, Aging

ABS 505

EFFECT OF PROCESS PARAMETERS ON THE MICROSTRUCTURE AND EFFICIENCY OF A TUBULAR ALUMINA CATALYST DOPED BY PLATINUM

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The use of hydrogen as a clean fuel has many complications in the production, storage and conversion of energy. The selective oxidation of carbon monoxide gas using the platinum / alumina catalyst can solve this problem. Meanwhile, the preparation of a suitable alumina catalyst base and the effective coating of platinum particles on its surface increases the conversion efficiency. The purpose of this paper is to provide a high level aluminous substrate using an aluminum alloying method and coating it with platinum particles. There are two stages of work, aluminum anodization in sulfuric acid or oxalic acid solution and optimization of its parameters to reach the alumina tubes with different diameter and wall thickness, in which optimum applied voltage, electrolyte concentration and induction conditions were performed. The study was performed at this stage using scanning electron microscopy and data related to the special surface. In the next step, nanoparticles of platinum are impregnated in different amounts using a suitable metal salt, solvent and surfactant using a more chemical method. After drying and calcining at temperatures of 400-600 ° C, absorption tests, degradation and microscopic examinations were performed on the specimens. Finally, the optimum conditions for the preparation of the catalyst were obtained to reach the maximum surface coating of platinum on the surface of alumina.

Keywords: Anodizing, Alumina, Catalyst

ABS 489

APPLICATION OF DIFFERENT MATERIALS FOR LAYERS OF ANODE SUPPORTED SOLID OXIDE FUEL CELLS PREPARED USING LARGE-SCALE CAPABLE PRODUCTION METHODS

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The development and fabrication of anode-supported solid oxide fuel cells (AS-SOFC) started in the Ceramic Department (CEREL) of Institute of Power Engineering (IEN) 10 years ago. The standard cells are based on 8YSZ electrolyte and LSCF cathodes, and are designed to operate at nominal temperature of 800°C. In order to produce anode supported solid oxide fuel cells at the industrial scale, low-cost and fast methods with high repeatability are under continuous development. For the preparation of thin layers screen printing is used. Porous anodic support of AS-SOFCs is yet produced using high pressure injection moulding (HPIM) which was recently implemented. Significant advantages of HPIM include automated fabrication, high precision, and negligible volume of waste Ni-based material.

During recent years, R&D activities of IEn were focused on the improvement of electrical and electrochemical parameters of cells and their components with main goal to lower the operating temperature using advanced materials for functional layers. In case of the electrolyte layer, scandia-doped zirconia was selected as the ionic conductor with enhanced conductivity, making possible to decrease the ohmic losses in a cell. Starting from scandia-doped zirconia, IEN has developed technology for fabricating dense electrolyte layers using ternary solid solution 10Sc1CeSZ. This material demonstrated three to four times higher ionic conductivity in comparison to the traditional 8YSZ, and lower degradation rate during long-term characterization under standard operating conditions of SOFCs. In the case of cathodic layer, complex oxides with perovskite structure (LSCF) were under consideration.

Presentation includes results, related to AS-SOFC with different functional layers with dimensions of cell up to 100x100mm and thickness in range of 550-1000µm. The properties of each functional layer are controlled by morphology of source powders, composition of the paste for screen-printing, and the thermal treatment. Characterization of cells includes both the microstructural analyses such as SEM with EDS and the methods of solid state electrochemistry. Performance of the newly fabricated cells was investigated in fuel cell (SOFC) and electrolysis (SOEC) IV-scanning and impedance spectroscopy in temperature range of 700-800°C under current density in excess of 1000mA/cm2 in SOFC, and up to -1.9A/cm2 in SOEC-mode.

Acknowledgment

This work was co-financed by the European Regional Development Fund under the Operational Programme Smart Growth (agreement no. POIR.01.02.00-00-0013/16-00) through project NewSOFC–“New designs, materials and manufacturing technologies of advanced solid oxide fuel cells” and by the Ministry of Science and Higher Education of the Republic of Poland through the statutory grant CPE/017/STAT/19

Keywords: SOFC,SOEC,HPIM

ABS 488

INCREASING THE RATE CAPABILITY OF HIGH ENERGY ELECTRODES FOR LITHIUM-ION BATTERIES BY LASER MACHINING

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It still is a big challenge to combine a long driving range with fast charging capability of electrical vehicles. In other words, it is extremely demanding to achieve both elements in Lithium-Ion batteries that are widely used nowadays, namely a high energy density and a high power density. Among others, the microstructure of the electrodes plays a key role to overcome this conflict of objectives. On the one hand, cell producers strive to increase the loading level and reduce the volume of the electrodes by compaction to increase the energy density. On the other hand, a good wettability of the electrodes by the ion conducting electrolyte, as well as continuous pore paths for the Lithium-ion diffusion, has to be ensured. As published in earlier work, electrodes with a homogenous microstructure are rather unsuitable to tackle this challenge: The thicker the electrodes and the more densified, the more the mobility of the Lithium-ions is restricted – and hence, the rate capability will deteriorate.

In this work, we investigated a laser based surface treatment of electrodes in order to enhance their kinetic properties. In the presentation, we are going to provide insights into the laser processing and to report electrochemical data of the laser processed samples. Due to an appropriate laser treatment, strongly densified electrodes achieve a higher discharge performance of up to approximately 20 % at high current rates compared to the unmodified ones. At the same time, there is no capacity loss at low current rates, since the laser processing supposedly does not affect the active material. In addition, we are going to present preliminary results of the long term stability of such electrodes. Beside the electrochemical data, we are going to provide information about the laser settings and processing itself as well as microstructural investigations, among others by Scanning Electron Microscopy. The microstructural studies were indispensable to identify proper laser parameters in order to avoid undesired modifications of the electrode such as melting or ablating of active material.

The study focuses on NCM based cathodes.

Keywords: Lithium-Ion batteries, energy and power density, laser machining, microstructure

ABS 475

ENHANCED CERAMIC PROCESSING SURROGATES FOR RADIOISOTOPE POWER SYSTEM (RPS) FUEL PELLETS BASED ON MIXED ALUMINA/CERIA COMPOSITIONS

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Due to various safety and other considerations, the U.S. currently employs plutonium-238 in the form of 238PuO2 ceramic pellets as the energy source in Radioisotope Power Systems (RPS) used in the exploration of the Solar System; such as the MMRTG (Multi-Mission Radioisotope Thermoelectric Generator) which currently supplies all of the electrical power for the Curiosity rover on Mars. It is anticipated that a future European RPS design will also utilize a ceramic fuel form employing the radioisotope americium-241. A RPS converts the decay heat released from the selected radioisotope into electrical power for the space mission.

Understanding the processing characteristics of the selected ceramic fuel form is one common technical endeavor for both the European and U.S. RPS programs. While it would be ideal to perform RPS fuel processing experiments with the selected heat source radioisotope, due to radiological, cost, materials availability, and other considerations the employment of a non-hazardous and non-radioactive surrogate material could greatly ease this field of study. Identifying a cold surrogate material, that as closely as possible mimics the processing characteristics of the selected radioisotope, will enhance future development studies in support of both European and U.S. RPS activities. This paper investigates the advantages of mixed alumina/ceria compositions as a possible enhanced ceramic cold processing surrogate which could be employed in support of both respective RPS endeavors.

Keywords: Ceramic processing, Cold surrogate ceramic, Radioisotope Power System

ABS 467

Si-Sn FILMS DEPOSITED AT DIFFERENT VACUUM PRESSURE USING RF MAGNETRON SPUTTERING AS POSSIBLE CANDIDATES FOR APPLICATION IN Li-ION BATTERIES

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With a continuous decrease in the size of electronic devices, the demand for batteries having greater capacity and better performance has also increased. In lithium-ion batteries (LIBs), the lithium ions travel from the cathode to the anode during charging via an electrolyte, creating large amount of vacancies at the cathode. The Li-ions are inserted at the anode occupying interstitial sites. The opposite happens during discharging. Generally, graphite is used as anode material. Specific capacity of graphite is 372 mAh g-1 whereas specific capacities of Silicon and Tin are 3579 mAh g-1 and 994 mAh g-1 respectively. The main drawback is the large volumetric change (297% and 257% for Si and Sn, respectively) during continuous cycles of charging and discharging [1]. Amorphous and porous structure is more resistive to fractures and pulverisation during charging and discharging of films [2]. A Porous structure helps in accommodating the expansion of volume during the cycles, resulting in good performance and long battery life. Tin is used as an alloying element because it forms an interpenetrating microstructure with silicon, resulting in higher specific capacities and better cyclability [3].
In this work, Si-Sn thin films were deposited by varying the tin content (power used for tin targets during depositions was 25W, 50W, 75W and 100W and the power for silicon target was kept at constant value of 400W for all depositions). The main idea is to obtain films which are simultaneously amorphous and porous, and consequently good candidates for LIBs. Two sets of samples were prepared using two different vacuum pressures 1.0*10-2 and 6.0*10-3 mbar. The films deposited at 1.0*10-2mbar were found to be amorphous, columnar and porous in nature, while the remaining-ones were more compact, consequently the first ones are promising candidates for LIBs-anodes. These results were confirmed using XRD, SEM, AFM and nano-indentation.

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Keywords: magnetron sputtering, amorphous silicon, porous composites

ABS 443

ION IMPLANTATION, MICROMECHANICAL TESTING, AND RESIDUAL STRESSES IN REACTION-BONDED SILICON CARBIDE FOR FUSION REACTOR BLANKETS

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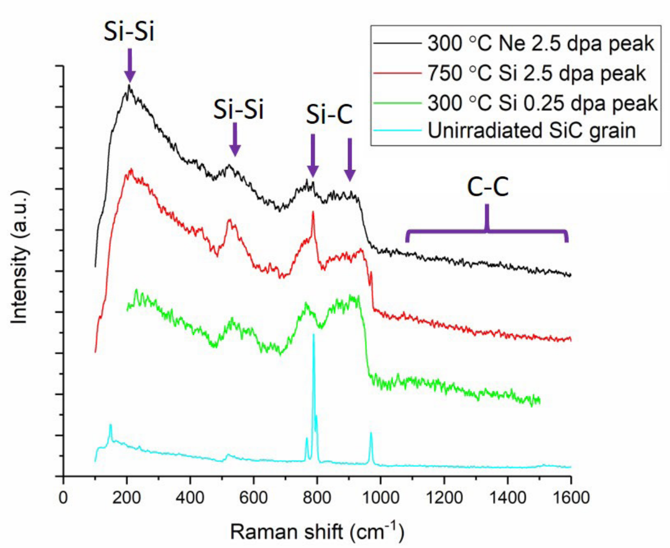
Objective Complex shaped components can be manufactured from reaction-bonded silicon carbide (RB-SiC) on a large scale at a more economical price compared to other forms of SiC. In unirradiated form, RB-SiC has suitable properties for the blanket of nuclear fusion power stations, however little is known about the effects of high-energy, high-temperature irradiation on this material in the context of a fusion blanket.

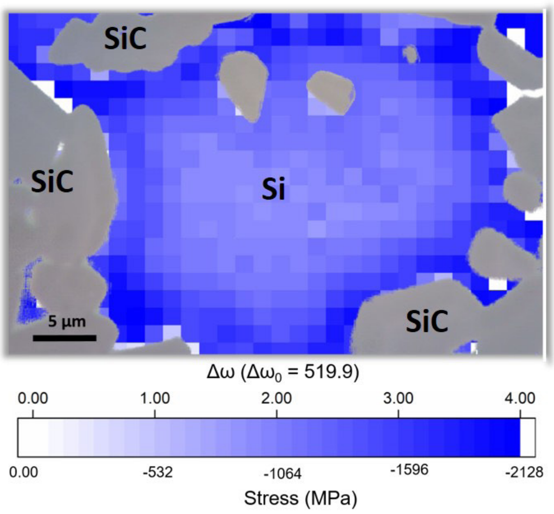
Materials & Methods Commercial grades of RB-SiC and novel forms of metal-silicide RB-SiC have been ion implanted to simulate radiation damage. Micromechanical properties have been studied using instrumented nanoindentation, and radiation-induced defects by Raman spectroscopy. Residual stresses have been measured using Raman spectroscopy and high-resolution electron backscatter diffraction mapping. Cross-sectional FIB tomography of nanoindents is used to investigate sub-surface crack morphology.

Results Large, spatially varying, processing-induced residual stresses have been identified in RB-SiC, which are redistributed due to the effects of radiation damage. Irradiation with different ions to the same nominal dose can cause different changes in mechanical properties and radiation defects. Higher temperature irradiation reduces the effect of the same nominal irradiation dose. Comparisons are made between dual phase RB-SiC and single crystal SiC and Si reference samples to give insight into the effect of microstructure on radiation damage. Cross-sectional FIB tomography shows changes in crack morphology caused by ion implantation, and HR-EBSD elucidates the effect of radiation defects on deformation around indents.

Conclusions Radiation-induced changes to the properties of RB-SiC are presented in the context of a fusion blanket application. Microstructural optimisation and reactor blanket design can mitigate degradation of properties. Using ion implantation to simulate neutron irradiation has some well-known drawbacks, enhanced for ceramics where chemical effects can be significant. New insights into the residual stresses in RB-SiC are presented which has implications in a variety of non-nuclear applications including aerospace.

Keywords: Micromechanical testing, Ion irradiation, Residual stress





ABS 441

SELF-SUPPORTED AND BINDER-FREE LFP/C THICK ELECTRODES PRODUCED BY POWDER EXTRUSION MOLDING AS CATHODES FOR Li-ION BATTERIES

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Renewable energies are considered the most promising alternative for energy production, because they are virtually unlimited and reduce the environmental impact. Among them, solar and wind energies are the most widely available ones. As the present electric-power grid has limited storage space, it is needed to develop massive energy storage systems. In this context, lithium-ion batteries (LIB) are an excellent technology due to (1) high energy density (2) portability (3) long cycle life and (4) zero emission of greenhouse gases. However, conventional LIB are limited to low temperature applications (less than 100 C) and are not suitable for specific applications, such as roof-top photovoltaic power stations which operate in a much broader temperature range. Following our previous work, where we applied Powder Extrusion Molding (PEM) for manufacturing of ceramic layer with thickness as high as 500 microns of LTO anodes with high electrochemical performances for LIB anodes [1], We applied this easy and scalable manufacturing method to produce binder-free solid thick LiFePO4 (LFP) cathodes. LFP was selected as cathode due to its important advantages: (1) low cost, (2) environmentally benign, (3) non-toxicity, (4) high theoretical specific capacity, (5) high cyclability and (6) high charge/discharge rates. Thus, LFP cathodes were produced by PEM, structurally characterized and tested in half-cells. The extruded electrodes present high mechanical consistency, homogeneous and porous microstructure and excellent electrochemical properties. The cathodes show high reversible specific capacity (> 150 mA·h/g) at C/10 with good capacity retention over 15 cycles at C/10 and C/5. Moreover, due to the absence of additives, the self-supported LFP electrodes have remarkable high volumetric capacity (370 mA·h/cm3 at C/10). Thus, LFP cathodes are attractive candidates for designing high energy LIB and could operate under high temperatures, avoiding binder degradation problems.

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Keywords: Li-ion batteries, electrodes, powder extrusion moulding

ABS 402

MXenes FOR NiB ANODES: ELECTROCHEMICAL BEHAVIOR AS A FUNCTION OF PROCESS PARAMETERS

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The development of suitable storage devices based on low-cost technologies and abundant materials is fundamental for a better exploitation of the growing energy production due to the non-programmable renewable sources. In the field of electrochemical storage, the current advantages (high volumetric and gravimetric capacitances) shown by lithium-ion batteries (LIB) collide with the limited natural abundance of certain elements involved in this technology (e.g.: Li and Co); Rechargeable sodium batteries (NIB) are regarded as complementary energy storage technology to LIB [1]. One of the main constrain that limit the mass diffusion of NIBs is their low electrochemical performance limited by the low stability and capacity of the best anodes like "Hard Carbon" [2].
Recently, MXenes [3], a new class of 2D materials obtained by the chemical exfoliation of carbides, known like MAX phase, have been proposed for hybrid NIB devices [4]. Ti-C based MXenes tested as anodic materials in hybrid NIBs show good specific capacity, long stability and rate capability extended on a large C-rate range. The lamellar structure of MXenes facilitates the intercalation of many alkaline and earth-alkali metal ions, on an extended range of charge-recharge rates for thousands number of cycles [5].
In this work, the preliminary results about the development of an integrated Lab-scale process from MAX Phase synthesis to NIB half-cell testing, will be shown and commented (see Figure 1).
To validate the real potentiality of these 2D compound like anodic materials for NIB, a complete control of each steps in MXenes production has been considered to be the best tool to correlate and maximize the storage performance.
The electrochemical properties of MXenes for storage applications have been studied as a function of some critical parameters in the different productive steps; particular attention like The effect on each productive step will be commented and correlate with the electrochemical properties of MXenes (Figure 2).
In our approach, Spark Plasma sintering (SPS) has been optimized to produce high pure TI-Al-C MAX-phases. In particular, our attention has been focused on the effects of the load and the partial pressure of inert used during the SPS production of MAXphases.

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Keywords: MXenes,Spark plasma sintering, anodes for Sodium-ion battery

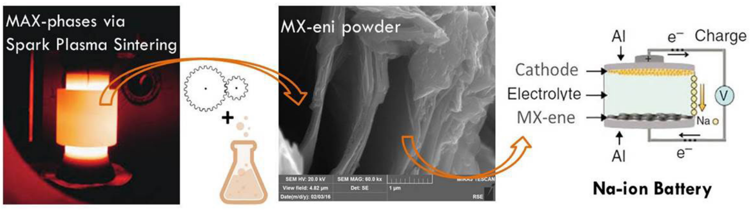

Figure 1: Schematic sketch of the flux of activity carried out in this work to obtain a MXene-based NIB

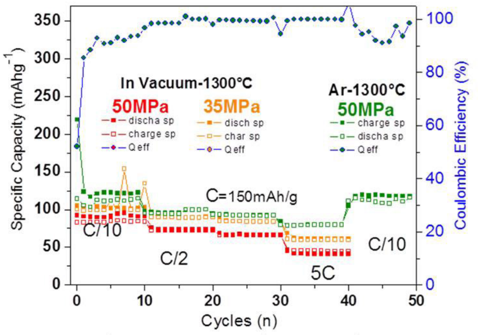

Figure 2: Specific capacity as a function of SPS parameters (Pressure and atmosphere) for MXenes based anodic electrods test in NIB half-cells

ABS 2

INVESTIGATION OF PALLADIUM-DOPED PEROVSKITE OXIDES FOR APPLICATION IN SYMMETRIC SOLID OXIDE FUEL CELL

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Objective Palladium-doped lanthanum strontium ferrites were investigated for anode and cathode applications in solid oxide fuel cells (SOFCs).

Materials & Methods La(1-x)Sr(x)Fe(1-y)Pd(y)O3±δ (x=0.4, y=0.05, 0.1) labeled as LSFPd4005 and LSFPd4010 were prepared by citrate auto-combustion method. The properties were investigated in oxidizing and reducing conditions. Structural and microstructural characterization were carried out by XRD, TEM and EDX analyses and EIS and polarization measurements using La0.8Sr0.2Ga0.8Mg0.2O3 (LSGM) pellets as supporting electrolyte were performed to evaluate the electrochemical performance.

Results The XRD patterns of the synthesized powders revealed an orthorhombic phase and a secondary phase of 2% mol PdO was detected for LSFPd4010.

For anode applications the redox stability was deeply investigated through a cycle of reduction and oxidation steps (Fig.). The reduction process causes the formation of SrLaFeO4 Ruddlesden-Popper (RP) phase, metallic Fe and Pd. A structural reversibility to perovskite phase was revealed by switching back to air. The reversible behavior was: exsolution of nanometric metal particles under reducing conditions and re-incorporation of cations into the perovskite structure in oxidizing conditions. This self-regenerating behavior mitigates the coarsening of metal nanoparticles at high temperature that is one of the main issues for cell degradation based on anodic cermets.

For cathode application, pellets conductivity and area specific resistance on LSGM electrolyte were measured. The electrical conductivity value in air was 130 S/cm for LSFPd4005 revealing a typical mixed ionic and electronic conductivity, i.e. a thermally activated behaviour at T<500 °C and a conductivity decrease on heating due to the progressive oxygen loss that lowers charge concentration and mobility.

Fuel cell tests in presence of H2 showed promising performances, since 350 mW/cm^2 were recorded at 750°C and after a series of redox cycles (120h) the current density remained almost unchanged with an average value of 0.38 A/cm^2.

Conclusions LSFPd shows a self-regenerating redox behavior promising for anode application. The capability of exsolved metallic nanoparticles (reducing conditions) to be re-incorporated into the perovskite structure (oxidizing conditions) avoids the coarsening of electrocatalytic sites promoting the cell stability. Moreover, it shows promising performance as cathode materials. Thus, LSFPd seems to be a valid candidate for symmetric SOFCs application.

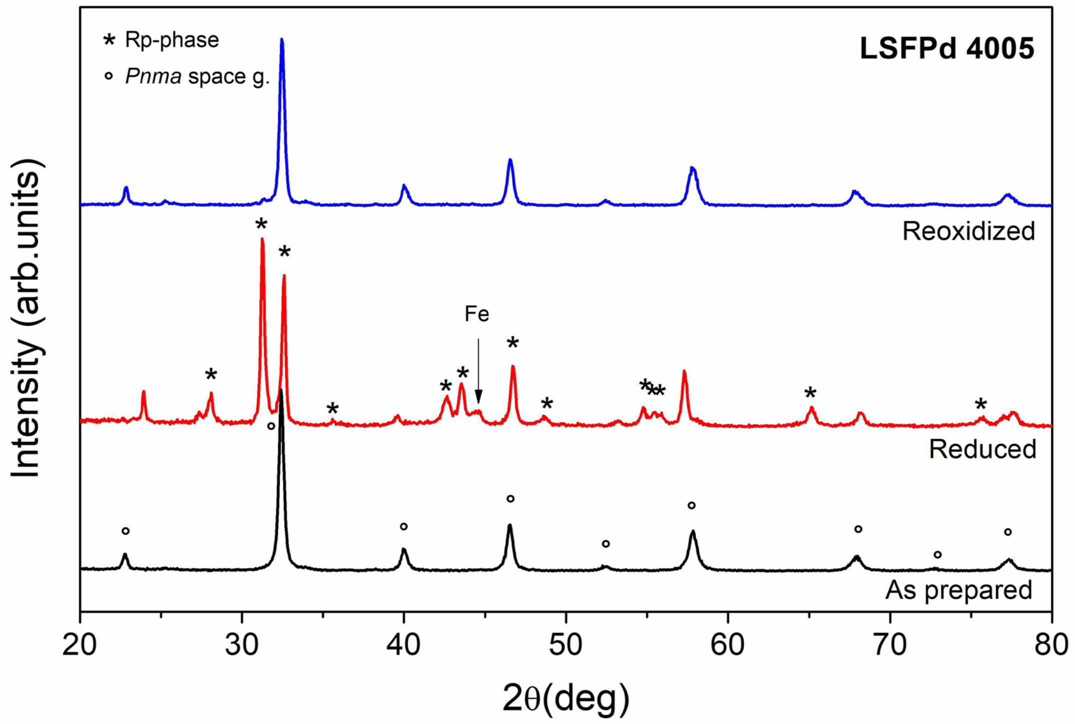

Fig. XRD patterns of thermal treated LSFPd 4005 powders

Keywords: Pd-doped perovskite oxides, Redox stability, Symmetric cells

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PRODUCTION OF AN ALL-CERAMIC ASYMMETRIC MEMBRANE WITH SUPERIOR HYDROGEN PERMEATION

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Mixed proton and electron conductor ceramic composites are among the most promising materials for hydrogen separation membrane technology especially if designed in an asymmetrical configuration (thin membrane supported onto a thicker porous substrate). However a precise processing optimization is needed in order to effectively obtain planar and crack free asymmetrical membranes with suitable microstructure and composition without affecting their hydrogen separation efficiency. This work highlights for the first time the most critical issues linked to the tape casting process used to obtain BaCe0.65Zr0.20Y0.15O3-δ - Ce0.8Gd0.2O2-δ (BCZY-GDC) asymmetrical membranes for H2 separation. The critical role of the co-firing process, sintering aid and atmosphere was critically investigated. The optimization of the production strategy allowed to obtain asymmetric membranes constituted by a dense 20 μm-thick ceramic-ceramic composite layer supported by a porous (36 %) 750μm -thick BCZY-GDC substrate. The asymmetric membranes here reported showed H2 fluxes (0.47 mL min-1 cm-2 at 750°C, feeding the 50% of H2 in He) among the highest obtained for an all-ceramic membrane (Figure 1).

Keywords: BCZY-GDC, Tape casting, Hydrogen separation

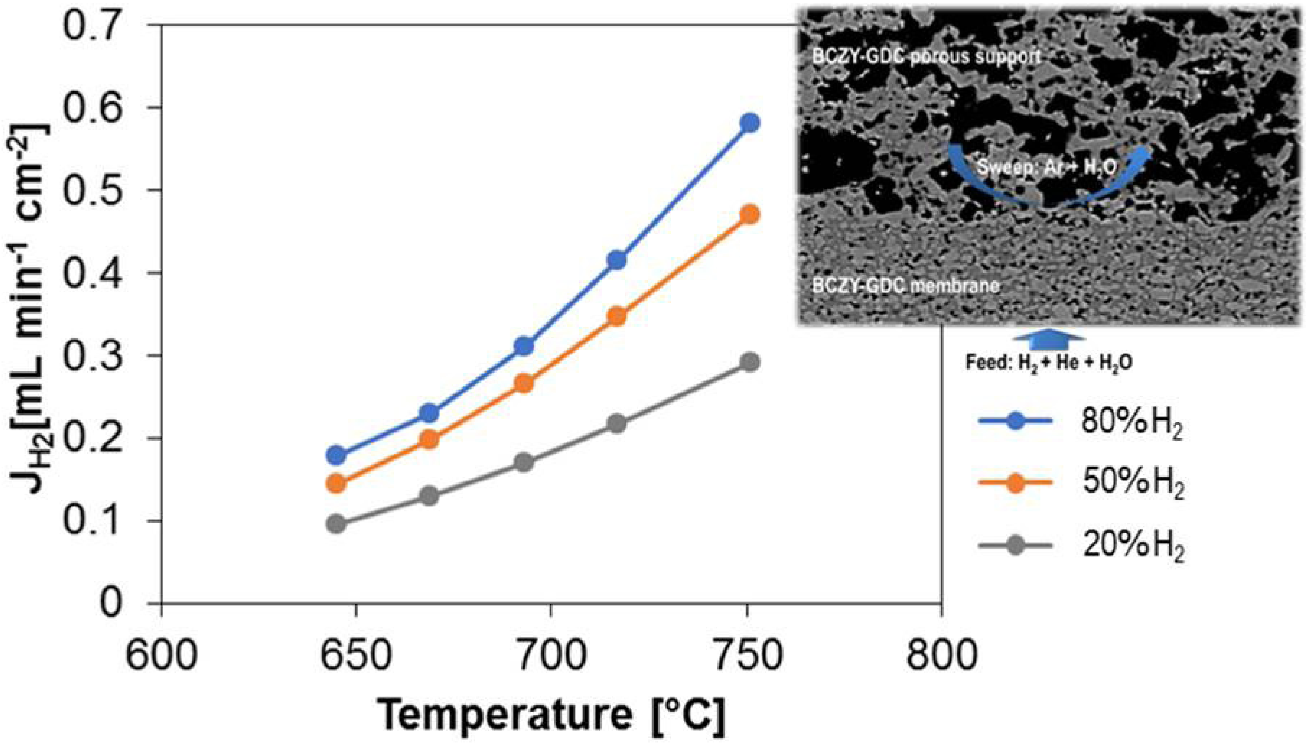

Figure 1 H$_2$ flux (mL min^{-1} cm^{-2}) as a function of temperature and H$_2$ partial pressure for BCZY-GDC asymmetrical membrane.

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STRUCTURAL AND MECHANICAL STABILITY OF $BaCe_{0.65}Zr_{0.2}0Y_{0.15}O_{3-\delta}$-$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ COMPOSITE HYDROGEN SEPARATION MEMBRANE UNDER IN-SITU REDUCING CONDITIONS

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Objective BaCe0.65Zr0.20Y0.15O3-d-Ce0.85Gd0.15O2-d (BCZ20Y15-GDC15) is considered a promising membrane for H2 separation at T > 600 °C. [1-3] This composite selectively separates H2 by incorporating charge protonic defects and electrons/holes that are transported to the opposite side of the membrane under a PH2 gradient. [4] However, long-term stability is a critical issue due to structural and mechanical alterations or chemical reactions that could occur under reducing environments. [4] This study investigated the phase stability of BCZ20Y15-GDC15 crystal structure under H2 atmospheres.

Materials and methods BCZ20Y15, GDC15 and BCZ20Y15-GDC15 dense samples were prepared as described in [1]. XRD analyses were performed at DESY Synchrotron (Hamburg) from RT to 800°C under dry and wet H2. Raman spectroscopy at high temperatures and conventional temperature programmed experiments (TPR, TGA) were conducted under reducing conditions.

Results BCZ20Y15 displays similar behavior under dry and wet H2: it is orthorhombic from RT to 180°C, rhombohedral up to 750°C and cubic until 800°C. GDC15 exhibits a cubic structure at all tested conditions. On the other hand, a synergistic effect of the two phases was revealed in the composite: indeed, BCZ20Y15 and GDC volumes tend to approach each other, mainly under wet H2; moreover, the BCZ20Y15 transitions occur at lower temperatures compared to single phase. RAMAN, TPR and TGA analyses confirm these observations, providing further details on redox properties of the composite.

Conclusions The phase stability of BCZ20Y15-GDC15 material was investigated by a powerful combination of in-situ synchrotron XRD with TGA, TPR and RAMAN analyses. This approach gives insights into the nature of interactions between the composite's phases, revealing a beneficial synergism that can mitigate the mechanical strains related to the operating conditions.

Acknowledgements
The thank C. Horstmann, G. Gizer and J.-C. Tseng for their help with synchrotron measurements and V. Zin, F. Agresti, C. de Leitenburg and E. Aneggi for their help with XRD data. This work has been funded by the MiSE-CNR Agreement 2015-2017 "Ricerca di Sistema Elettrico Nazionale".

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[5] C. Mortalò Et al., J. Membr. Sci. 564 (2018) 123.

Keywords: Structural stability, Composite, MPEC conductors

ABS 326

CEMENTED CARBIDES AS CANDIDATE MATERIALS FOR HIGH-HEAT-FLUX APPLICATION IN FUTURE FUSION REACTORS

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Development of fusion power plants is one of the greatest scientific and technological challenges. While the last experimental reactor ITER is under construction, designing of Demonstration power plant (DEMO) is already undergoing. In order to achieve high efficiency and safe operation in the DEMO, where conditions will be more severe than in ITER, it is necessary to provide suitable structural materials. Development of low activation materials, which would withstand the high-heat-loads in the divertor without critical damage and significant activation, is one of the priorities of the European fusion programme. Current research has been focused on the improvement of tungsten, which has certain limitations. As an alternative, we propose tungsten carbide (WC) based cemented carbides with a low-activation binder phase (e.g. Fe or/and Ni) or a high-entropy alloy (HEA). Namely, in contrast to W metal, WC is not subject to recrystallization at high temperature. This might provide a new opportunity to increase the heat flows in the divertor, leading to a more cost-effective process. The objective of the research is to select a suitable binder metal or alloy to provide sufficient toughness to the composite material.

The WC-based cemented carbides were prepared by mixing WC powder with a binder phase: a) HEA or b) Ni, Fe, NiFe alloy or Co powder. The alloys with different compositions were prepared by melting in a vacuum induction-melting furnace. Powder mixtures with binder phase content up to 10 wt % were sintered in Spark-Plasma-Sintering device at 1350 °C for 5 minutes at 60 MPa. Characterisation of sintered materials involved microstructural analysis and measurements of flexural strength, E-modulus and Vickers hardness. The samples of cemented carbides prepared from nanosized WC and binder metal from the iron group were all successfully sintered to high density. As expected, the best results (100 % density and flexural strength >1800 MPa) were achieved for WC-Co, which was used only as a reference, as Co is not allowed in fusion-relevant materials due to high neutron-activation. Addition of iron as a binder resulted in corrosion, similar, although less prominent, appeared for Fe-Ni alloy. On the other hand, WC-Ni reflected promising results. It was found that cca. 10 wt.% of Ni is needed for full densification, and flexural strength was >1700 MPa. Thermal conductivity of the material was ~50 W/mK, which is lower than expected and needs. Among the HEA, AlCrMoNbTiV appear the most promising and will be subject to further analysis.

Keywords: cemented carbide, WC, DEMO

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DEVELOPMENT AND CHARACTERIZATION OF NEW METAL EXSOLUTED PEROVSKITES AS SOFCs ELECTRODES

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The "solid phase crystallization" procedure provides [1] an alternative and valuable synthesis method for new energy SOFCs electrode materials. Its simplest description considers the presence of metal precursors homogeneously distributed in the potential electrode material that, after calcination and reduction, yields in situ finely dispersed and stable metal particles by exsolution from the former material. These metallic particles can participate in the electrode reactions. Thus, the segregation control and growing of these metallic particles onto the active surface material open a new procedure to reach alternative and cost-effective electrode materials [2]. Such tailored materials would enhance catalytic, electrical and electrochemical properties of the redox processes involved in the electrodes of high temperature fuel cell. Furthermore, they will improve the device durability and reduce performance losses due to the decrease of sintering and coking phenomena [3-5].

We have synthesized and obtained new materials and their corresponding metal exsoluted ones based on the general perovskite formulation La1-x-zSrx{ }zTi1-yMyO3-δ (0 <= x <= 0.4, 0 <= z <= 0.2, M = Ni and/or Fe and { }=vacant). Currently this research continues to simultaneously explore the limits of the aliovalent substitution and charge compensation mechanism combined with their metal segregation trends. Materials are characterized under oxidizing and reducing conditions (see Figure 1, below). The degree of exsolution process and composition of nanoparticles at different temperatures was evaluated by TEM and SEM, while EIC is used to characterize the electrochemical performance of pristine and ex-soluted materials. Evidences of exsolution under reducing atmospheres appear above 900°C

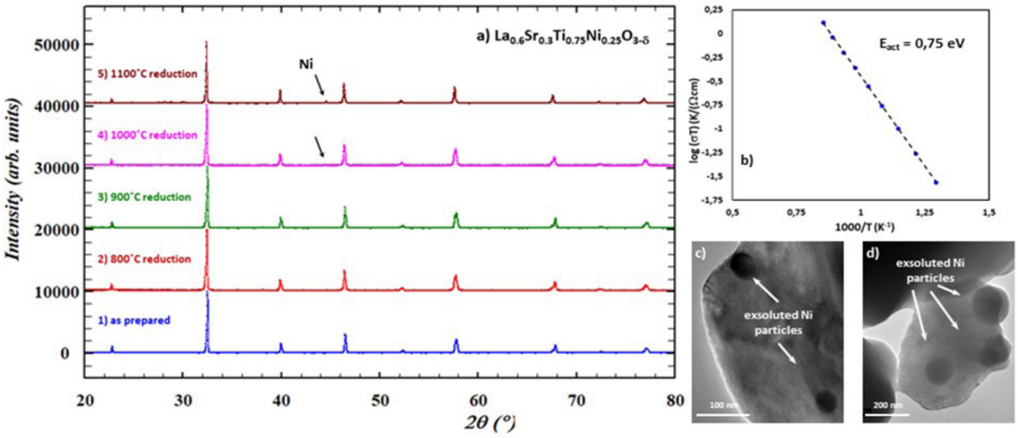

Fig. 1: a) Diffraction patterns of the A-vacant La0.6Sr0.3Ti0.75Ni0.25O3-δ compound (arrow points (111) diffraction peak of segregated Ni metal); b) corresponding impedance spectroscopy under oxidizing conditions; c) and d) TEM micrographs of reduced samples at 1100°C and 1200°C, respectively.

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Keywords: metal ex-solution, in situ nanoparticles growing, perovskites

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BIOMIMETIC 3-DOM CERIA ECOCERAMICS FROM SUSTAINABLE CORK TEMPLATES FOR SOLAR THERMOCHEMICAL CO_2 SPLITTING

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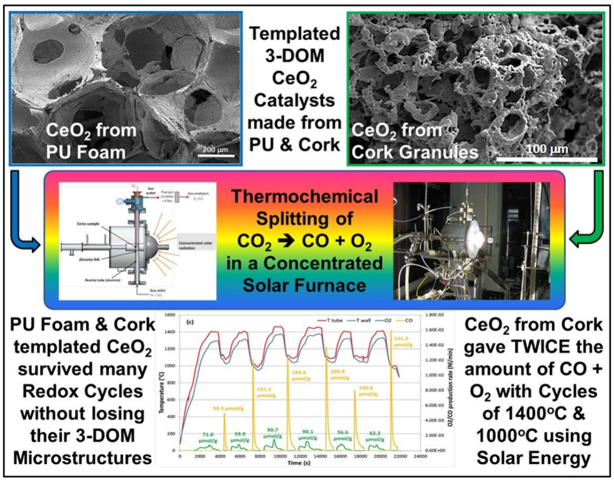
Climate change and renewable energy sources are two of the major technological and societal challenges of the millennium, and one emergent technology that can contribute to the solution of these problems is thermochemical energy production using solar power. This process uses very high temperatures (1600 oC) to split water or CO2 and produce hydrogen or CO. Nevertheless, current solar-to-energy efficiency levels are modest, which is a major challenge limiting this technology. Among the materials that have been investigated for thermochemical fuel production (TCFP), cerium oxide (CeO2) is the benchmark material. CeO2 has excellent redox properties and oxygen storage / release capacity. However, its low reduction and oxidation rates hinder the efficiency of thermochemical fuel production. Process kinetics can be modified by increasing CeO2 surface area and porosity, suggesting that three-dimensionally ordered macroporous (3-DOM) CeO2 could further enhance systems efficiency. We addressed the two-step solar thermochemical production of CO from CO2 using concentrated solar power (CSP) to drive the redox reaction. In this work cork, a unique sustainable resource, was used as a template for producing lightweight and porous ecoceramics using a simple and green-chemistry procedure [7, 8]. The ceria ecoceramics preserved the 3-DOM microstructure of cork, but the cell rear walls were ruptured, thus increasing the open porosity and surface area. The use of cork-derived ceria ecoceramics for solar fuel production is innovative, and they exhibited a good ability to split CO2 to produce CO for use in synthetic fuels. Both ceria granules prepared from cork templates and ceria foams were investigated, and CO yields for the cork-based ceria granules were two times higher than for ceria foams. The ceria ecoceramics also had amongst the higher ever reported rates oif CO production, and the 20 micron cell size of cork templated ceria granules is critical for these enhanced reaction rates.

Keywords: Thermochemical CO2 splitting, Ceria CeO2 ecoceramics,3-DOM cork microstructure



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LONG-TERM STABILITY OF GLASS-CERAMIC SEALANTS FOR SOLID OXIDE CELLS AT RELEVANT CONDITIONS

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Glasses and glass-ceramics are often used as sealants in solid oxide cell (SOC) stacks and systems. Their ability to provide gas tightness, thermal and electrical insulation as well as an exceptional processing flexibility made them suitable for this application.

Long-term stability and high performance of SOCs are fundamental requirements for many energy applications. Sealants, as part of an SOC, must endure both, thermal gradients and mechanical stresses during the system lifetime. Therefore, long-term studies of sealant stability, in terms of chemical interactions, microstructure and thermal properties, are critical. Especially when assessing various material combinations and interfaces between adjacent system components, such as interconnects, frames and cells.

Three different glass ceramic sealants were subjected to a long-term test; two sealant commercial compositions from Schott AG, and a third composition, V11. The latter was recently developed in collaboration by the Technical University of Denmark (DTU) and the Politecnico di Torino (POLITO).

In the present work, Crofer22H and AISI 441 were chosen as interconnect materials. These interconnectors were preoxidized or aluminized in order to suppress chemical interactions with the sealant.

Small coupon samples were assembled simulating a single repeating unit of a SOC stack and tested by applying a temperature profile resembling the initial stack sealing conditions, in order to evaluate the compatibility of the sealant between an interconnect and a cell. Ageing times were set at 250h, 2500h and 5000h, applying a constant temperature of 750°C. In an SOC, sealants are exposed both to oxidizing atmospheres as well as to reducing atmospheres, hence, in this work the influence of different atmospheres on the sealant was also studied.

The stability of the sealant after ageing was verified by means of a scanning electron microscopy (SEM) aside from an energy dispersive X-ray spectroscopy (EDS) in order to investigate interactions between the sealants and the adjacent components. Finally, an X-ray diffraction technique was used to evaluate the crystallization of the sealants, and dilatometric measurements were performed to analyze thermal expansion variations after ageing.

Preliminary results indicate that the two commercial sealants crystallize over time and are still amorphous after sealing, while V11 crystallizes within the sealing procedure (15 hours) and its microstructure shows only slight variations after ageing. Therefore, since the sealant is stable, eventual interactions at the interface will have a large impact on the final result.

Keywords: sealant, long-term, SOC

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CONTINUOUS SYNTHESIS OF 2D HYDROXIDES FOR DIRECT PRINTING OF OER CATALYSTS

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Layered Double Hydroxides (LDH) are a group 2D-structured materials consisting of metal hydroxide layers stacked with negative anions. Bivalent and trivalent cations are distributed within the 2D hydroxides positively charged layers, requiring the presence of negative anions for compensating the charge excess. A wide variety of LDH compositions have been prepared using different metals both at the divalent site (Ca2+, Mg2+, Ni2+, Co2+, Mn2+) and trivalent site (Al3+, Fe3+, Co3+).

Among the others, Ni2+, Fe3+ and Co3+ containing LDHs have shown outstanding catalytic performance towards the Oxygen Evolution Reaction (OER), in terms of both activity and durability [1,2]. Due to these performance and availability of Ni, Fe and Co, these materials are emerging as promising candidates for application as oxygen electrode materials in electrolysis cells. However, most of the studies carried out so far are focused on the batch synthesis of NiCo and NiFe LDH, without considering preparation and processing on a large scale.

A scalable synthetic route for metal hydroxide nanoparticles is represented by continuous flow hydrothermal synthesis (CFHS). In this process, streams of reactants are constantly mixed within a reactor at high temperature and pressure. Here, we show our efforts in synthesizing NiCo and NiFe LDHs via CFHS, for the first time. The role of the different redox chemistries of Fe and Co was investigated, pointing out remarkable differences with batch processes, emerging from operating in a kinetic control regime. In particular, the NiCo LDH structure could not be achieved, but only a solid solution of Ni2+ and Co2+ hydroxide was formed. Conversely, the LDH structure was obtained using Ni2+ and Fe3+, and the particular conditions of the CHFS led to the formation of extremely small platelets with a diameter of 50 nm and thickness < 3nm.

For processing the as-produced particles, the CHFS dispersions were converted into inks for deposition by inkjet printing. This approach allowed the deposition of thin films of catalyst, controlling the amount of material deposited and minimizing the catalyst utilization. Therefore, for testing the material activity towards OER, 500 nm thick films of NiFe LDH were deposited on carbon electrodes. The printed samples were tested in alkalyne conditions, demonstrating that the material synthesized and processed with this scalable approach had a comparable activity with the NiFe LDHs reported in literature.

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Keywords: Layered double hydroxides, inkjet printing, continuous flow synthesis

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ULTRALOW THERMAL CONDUCTIVITY OF $(La_{1-x}Pr_x)_2Mo_2O_9$ DENSE CERAMICS

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Objectives A great interest lies in identifying low thermal conductivity compounds on account of their ability at increasing high temperature engines' efficiency while they could be used as thermal barrier coatings. Thermal barrier coating materials need to show a low thermal conductivity, an absence of phase transformation between room temperature and operating temperature as well as chemical inertness.
Lanthanum molybdate La2Mo2O9 and the related substituted compounds are widely studied for being used as a solid oxide fuel cell's electrolyte thanks to their high ionic conductivity. However, La2Mo2O9 shows as well a thermal conductivity lower than 1 W.m-1.K-1 [1]. The complete solid solution from La2Mo2O9 to Pr2Mo2O9 has been investigated, expecting to lower the thermal conductivity thanks to increasing the atomic mass on the La site and creating on-site entropy.

Material & method (La1-xPrx)2Mo2O9 powders have been synthesized by solid state reaction for x = 0.00, 0.10, 0.25, 0.50, 0.75 and 1.00. Dense pellets have been obtained by conventional sintering in air. Samples were characterized by X-ray diffraction, scanning electron microscopy. Their thermal stability and thermal conductivity have been studied with differential scanning calorimetry and laser flash analysis from 100 to 700 °C and their crystallographic structure has been investigated by Rietveld refinements.

Results La2Mo2O9 shows a alpha-monoclinic to beta-cubic structural transition at about 580 °C which is almost suppressed with a 50% substitution by praseodymium on the lanthanum site stabilizing the high temperature phase while reducing the thermal conductivity of La2Mo2O9 by 15%, reaching values lower than 0.85 W.m-1.K-1 over a large temperature range. When x reaches 0.75, a similar phase transition to that of La2Mo2O9 appears, this transition is attributed to a triclinic to cubic phase transition and the thermal conductivity increases.

Conclusion Thermal conductivities in (La1-xPrx)2Mo2O9 are affected by the substitution rate and the crystallographic structure. The 50% substituted compound is an excellent candidate to be used as a thermal barrier coating material as it reduces the thermal conductivity (lower than 0.85 W.m-1.K-1 corresponding to a 15% decrease compared to that of La2Mo2O9) and almost suppress the phase transition of La2Mo2O9.

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Keywords: Thermal barrier coatings, LAMOX, Thermal properties

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EFFICIENT AND CONTROLLED NANO-CATALYST SOLID-OXIDE FUEL CELL ELECTRODE INFILTRATION ASSISTED WITH CATECHOL SURFACTANTS

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Nanostructured solid oxide fuel cell (SOFC) electrodes can show enhanced power density with high catalytic activity owing to the higher surface area to volume ratio. However, maintaining the high surface area at elevated sintering temperatures is a well-known challenge due to inevitable microstructural changes such as particle coarsening. Wet impregnation/infiltration method is a practical and well-utilized method to form nanoparticles within the porous electrode microstructure of solid oxide fuel cells (SOFC) which requires relatively low calcination temperatures. Critical factors that impact the reduction of the electrode polarization using the nano-catalyst impregnation strategy include catalyst loading, decoration type, and volumetric distribution homogeneity through the porous electrode microstructure. These can mostly be tuned by performing repetitive infiltration cycles followed by a co-firing step after each cycle for calcination. However, this labor/time intensive repetition continues until the desired nano-catalyst loading is achieved. Major risks such as inter-particle interactions, pore-clogging, inhomogeneous deposition may result in gas diffusion related rapid cell voltage degradation issues.

In this study, a catechol-assisted, efficient nano-catalyst infiltration protocol that includes a single calcination step was developed for commercial anode-supported Solid Oxide Fuel Cell (SOFC) electrode. Catechol based molecules that have multi-functional end-groups such as benzene and hydroxyl groups, are capable of material-independent strong adhesion property when linked and polymerized. Dopamine (DA) is the most utilized monomer for functionalizing flat or highly porous membranes. However, DA undergoes uncontrolled aggregation during the polymerization stage. Hence, our research focused on the alternative catechol surfactants, norepinephrine, caffeic acid, cinnamic acid, and gallic acid to avoid potential pore clogging issues for the 3-D SOFC electrode architecture. Here, we first investigated the formation kinetics of adhered bio-surfactants on flat YSZ substrates under various conditions (solid loading, immersion time etc.) using atomic force microscopy (AFM) and UV- Visible Spectroscopy. Then the coated substrates were immersed into cerium nitrate solution. The ceria nuclei sites of fired samples were observed under different surfactant coating conditions. Finally, we demonstrated the use of polymerized alternative surfactants to the anode electrode of the commercial anode-supported button cells. A microstructural/performance correlation was developed by SEM and four probe impedance spectroscopy on 120 h operated cells under 0.5 A/cm^2 at 750 degrees Celcius. The two-step catechol surfactant-assisted infiltration resulted in homogeneous incorporation of a nano-catalyst film+island layer inside the electrode active area. The process achieved a lower electrode overpotential with enhanced stability.

Keywords: Catalyst, Electrode, Surfactant

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ELECTRICAL TRANSPORT IN SODIUM PHOSPHATE GLASSES CONTAINING TUNGSTEN AND MOLYBDENUM OXIDES

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Oxide glasses containing Li_2O or Na_2O in combination with transition metal oxide (TMO) have recently emerged as promising candidates for cathode materials in battery technologies. Such glasses exhibit mixed ion-polaron conductivity with the ionic contribution being dependent on the concentration and mobility of the alkali (Li^+/Na^+) ions whereas polaronic conductivity follows the small polaron hopping mechanism and depends on the amount of TMO and a relative fraction of TM ions in different valence states.
In this study, we report the influence of WO_3 and MoO_3 on the transport of sodium ions in phosphate glasses. Two series of glasses of molar composition $40Na_2O$-xWO_3-$(60-x)P_2O_5$ and $40Na_2O$-$xMoO_3$-$(60-x)P_2O_5$, x = 0, 10, 20, 30, 40, 50 mol%, were prepared by melt quenching. Electrical properties of glasses were measured by impedance spectroscopy over a wide temperature and frequency range. Raman spectroscopy was used for structural characterization, whereas the fractions of tungsten and molybdenum ions in different valence states were determined by EPR spectroscopy. The DC electrical conductivity of glasses changes non-linearly as P_2O_5 is gradually replaced by WO_3/MoO_3 exhibiting maximum at 40 mol% WO_3 (1.6 x 10-8 S/cm at 303 K) and 30 mol% MoO_3 (2.2 x 10-9 S/cm at 303 K). Raman spectra reveal that with the addition of WO_3/MoO_3, octahedral WO_6/MoO_6 units enter the phosphate network, gradually depolymerize metaphosphate chains and form tungstate/molybdate network. We propose that the observed conductivity enhancement of approximately four orders of magnitude originates from the modification of glass structure which has a favourable effect on the mobility of sodium ions rather than the contribution of polaronic transfer between tungsten or molybdenum ions in different valence states. Indeed, EPR study revealed that the fraction of W^{5+}/W_{tot} and Mo^{5+}/Mo_{tot} is less than 1% which suggest that the polaronic conductivity in these glasses is small. In conclusion, we show that the mixed-glass former effect can be extended to the glass systems where the conventional glass forming oxide (P_2O_5) is replaced by the conditional one (WO_3/MoO_3).

Keywords: oxide glasses, electrical conductivity, structure

ABS 178

DEVELOPMENT OF HIGHLY HYDROGEN SELECTIVE PALLADIUM-BASED MEMBRANES ON ASYMMETRIC POROUS, CERAMIC SUBSTRATES WITH HIGH SPECIFIC FLUX

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In Germany, hydrogen was produced with more than 50 % from natural gas and naphta [1]. Syngas, fabricated by steam reforming or direct gasification, contains a large amount of H2 and other components. H2 can be separated from the gas using a H2 selective membrane. There are large efforts to use metal membranes for efficient H2 separation [2]. Pd-based membranes seem to be suitable, because they combine several advantages namely, high oxidation resistance and their application in moderate temperature range. On the other hand, Pd is very expensive leading to high costs of the membrane. The main impact regarding membrane costs is the layer thickness.

This work focus on the fabrication of ultra-thin (less than 500 nm) Pd layers on asymmetric porous, ceramic substrates. Ceramic supports possess high thermal and chemical stability. The deposition of Pd layers was realized by wet chemical methods. With such thin layers material cost of Pd is in the same range as for the ceramic supports required and do dominate the total membrane cost any more. Additionally these thin membrane layers allow significant hydrogen permeances even at lower temperatures (150°C). This opens the field of membrane reactors for temperature sensitive fine chemicals.

For membrane preparation asymmetric porous alumina substrates in single channel geometry were used. The final silica layer possess a pore size of 1 nm. For preparation of Pd layers, C10H14O4Pd solved in CHCl3 was used. After drying step, a thermal treatment is required for membrane formation. The membranes were characterized by scanning electron microscopy and single gas permeation measurements.

First single gas permeation measurements indicate a highly selective membrane for hydrogen. The H2 permeance increased with increasing measurement temperature from 0.2 $m^3/(m^2hbar)$ to 0.9 $m^3/(m^2hbar)$. The ideal permselectivity of H2/SF6 increase from 8 to 46 respectively.

The first results show the high selectivity of the membrane and their high potential for H2 separation applications. FESEM investigations leading to an estimation of the layer thickness of approx. 200 nm. With increasing measurement temperature (room temperature up to 150 °C) exclusively H2 permeance increase, leading to conclusion, that the membrane contains small amount of defects and the rate determining step of separation is the Pd layer.

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Acknowledgements

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Keywords: Hydrogen, Palladium, Porous ceramic substrate

ABS 176

INFILTRATION-ASSISTED DENSIFICATION OF GDC ELECTROLYTE

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In contrast to conventional energy conversion methods based on burning of fossil fuels, solid oxide fuel cells (SOFCs) offer clean and efficient energy generation without environmentally hazardous emissions. As SOFCs are operated at elevated temperatures (700-1000 °C) the cost for the power generated is currently prohibitive to lend the method for widespread adaptation. A modified microstructure can help reduce this cost. Room for improvement exists in all cathode, anode and electrolyte layers. Anode supported SOFCs, for example, are fabricated by co-sintering of a Ni-gadolinia doped ceria (GDC) composite anode and GDC electrolyte layers. To ensure gas-tight electrolyte, and hence high open circuit potential, co-sintering must be performed at temperatures exceeding 1400 °C. While this temperature is perfect for obtaining a dense GDC electrolyte, the anode layer suffers from coarsening of the grains, resulting in short triple phase boundary length and thus low electrode performance. Therefore, there is a demand to reduce this firing temperature without compromising electrolyte density and electrical conductivity of the electrolyte.

In this work, infiltration of a polymeric GDC precursor solution into the previously heat-treated porous GDC scaffold is proposed to reduce the sintering temperature. The amorphous GDC film that forms as a result of infiltration on the particles of the porous GDC scaffold i) increases the coordination among the GDC particles and ii) provides a fast diffusion pathway. Density measurements show that heat treatment at 1200 °C followed by polymeric precursor infiltration results in relative densities of ca. 95 %. This corresponds to reducing the sintering temperature of GDC by 200 °C, without any additives that might influence the electrical properties. Electrochemical impedance spectroscopy (EIS) measurements performed on the GDC electrolytes densified by the aid of infiltration reveal that their ionic conductivity values are approximately the same as those densified by conventional sintering at 1400 °C. Open circuit potential of the GDC electrolyte prepared by infiltration-assisted sintering is determined to be in the range of the theoretical values. The outcomes of this study is considered to be useful to fabricate anode/electrolyte bilayers at lower temperatures and thus to increase the overall cell performance.

Keywords: Densification, Electrolyte, Infiltration

ABS 167

CHARGE STORAGE MECHANISM OF $Na_{0.44}MnO_2$ USING AS AN ACTIVE MATERIAL FOR AQUEOUS RECHARGEABLE SODIUM-ION STORAGE SYSTEMS

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Recently, as a renewable and sustainable energy storage technology, aqueous rechargeable sodium-ion storage systems have becoming a hotspot due to the environmental friendliness, safety and low cost. Not like conventional lithium-ion batteries, aqueous sodium-ion systems have many advantages for large-scale stationary electric storage, such as low cost of Na, its abundant resource compared to Li and the stable electrochemical performance. In addition, aqueous electrolytes are inherently safer and more eco-friendly than organic electrolytes. Although recently some new family of materials has been introduced, channeled structure Na0.44MnO2 (NMO) is still one the most promising candidate as cathodic materials for aqueous sodium-ion storage systems. It is because of its abundance and low price ($7.6 kg-1), relatively high theoretical capacity (121 mAh g-1), non-toxic, wide potential window in aqueous solutions(~ 1V) easily produced by different routes such as hydrothermal solid-state, sol-gel and polymer-pyrolysis . The mechanism of Na de/insertion of NMO in organic electrolytes has been exclusively studies. However, the behavior of NMO in aqueous media in quite different from organic ones. It was shown that the apparent diffusion coefficients of Na in Na0.44MnO2 were determined to be three order of magnitude lower in aqueous electrolytes. The differences evaluated were mainly ascribed to the charge transfer resistance and the additional resistance from the formed solid-electrolyte-interphase (SEI) layer that is not exist in aqueous media. Moreover, rate capability of NMO in aqueous electrolytes seems to be more stable than organic ones. Therefore, it is worth to shed more light on charge storage mechanism of this important active material in aqueous electrolytes.
In this study, energy storage mechanism of NMO in an aqueous electrolyte (Na2SO4, 1M) was thoroughly studied by means of electrochemical impedance spectroscopy (EIS) at different values of polarization and, current contribution in double layer, pseudocapacitance and diffusion were determined by a novel equivalent circuit system in different frequencies. For supporting the interoperations by EIS other electrochemical tests such as cyclic voltammetry (CV) at different scan rates as well as non-electrochemical analysis such as ex-sito X-ray diffraction (XRD), X-ray photoelectron Spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDS) were performed and results were compared. According to EIS interpretation, in low scan rates interested for battery applications, the diffusion contribution is far more dominant that was predicted by common methods such as CV.

Keywords: Storage mechanism, Sodium Manganese Oxide, Aqueous Na-ion batteries

ABS 143

ADDITIVE MANUFACTURING OF ZIRCONIA SCAFFOLD FOR HEAT STORAGE APPLICATION

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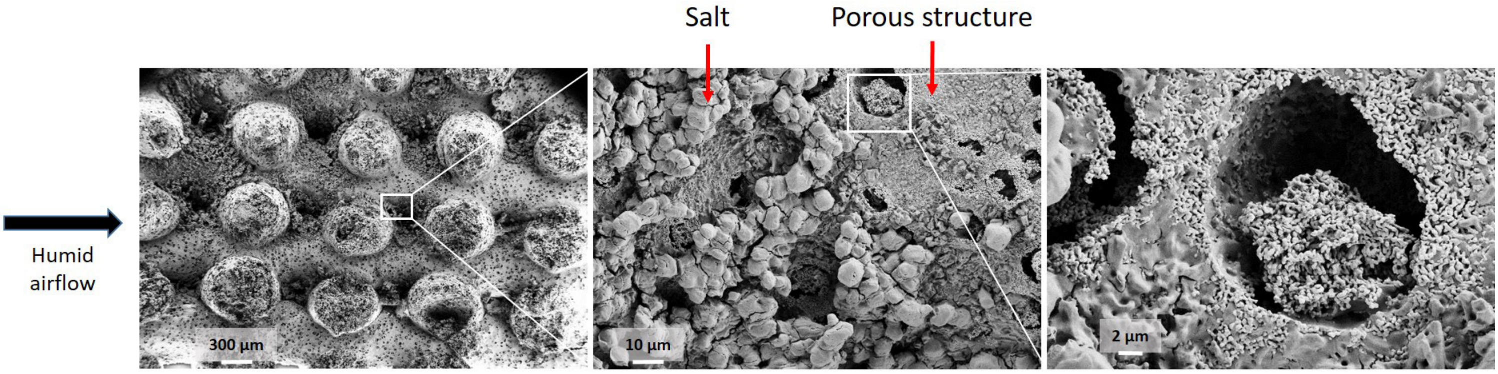
The aim of this work is to fabricate an efficient composite made of ceramic and hygroscopic salt for thermochemical heat storage application for buildings.

Some hygroscopic salt can provide or store a large quantity of heat by mean of hydration. But, due to agglomeration issues during their hydration, their performances are inhibited, therefore, those salts cannot be used alone. To overcome it, scaffold-like structures of zirconia were fabricated by additive manufacturing (robocasting) as a host material for the salt. The role of this porous host material is double: to allow the salt adhesion and avoid its agglomeration; to allow humid air flow distribution for its hydration. Composite is made by impregnation of a salt solution ($MgSO4,7H2O$) in the ceramic scaffold, followed by drying. In order to increase the amount of salt inside the host material and to allow its hydration by humid air flow passage, the ceramic structure was optimized by creation of porosity at different scales: in addition to the macroscopic porosity designed in the numeric model used for additive fabrication of the host material, partial sintering and addition of sacrificial fugitives were combined to create interconnected networks of porosity at filament scale (figure 1).

Mercury porosimetry was used to measure channel size and pore content at filament scale, revealing the presence of two different characteristic pore sizes: 0.1 µm, and 1 to 50 µm. SEM and local x-ray tomography revealed interconnection of porosity created by sacrificial fugitives. The hydration of the salt on the host material was followed in-situ with SEM under humid environment, revealing its swelling. Pores created by the partial sintering seem to allow the swelling of the salt thanks to its interconnected opened channel. Hydration/dehydration cyclability of this composite is currently studied, showing an almost complete reversibility up to 5 cycles, in accordance with the thermodynamical predictions, which is promising for heat storage application.

Keywords: thermochemical heat storage, additive manufacturing, multi-scale porosity



Composite ceramic/salt after 5 cycles of hydration/dehydration

ABS 141

POLYMER-DERIVED GROUP III-NITRIDE CERAMICS WITH UNIQUE HYDROGEN STORAGE PROPERTIE

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Recently, a great deal of research on hydrogen adsorption/desorption behavior of nanostructured carbon and III-V compounds has been undertaken both experimentally and theoretically. Among them, density functional theory studies on the nanostructured aluminum nitrides (AlNs) such as nanosheet and nanotube predicted an interesting hydrogen storage capacity due to their unique surface structure having electrically unsaturated three-fold Al element bonded with electron-rich N element which can be expected to offer desirable heterolytic dissociative adsorption sites for hydrogen molecules. In this study, as our experimental approach, various materials of group III-IV-V, systems were designed and synthesized, and the relationships between their structural/electrical properties and hydrogen adsorption/desorption behavior have been studied.

Ternary XCN and quaternary SiXCN (X = Al, Ga) were synthesized through polymer-derived ceramics (PDCs) route. Single source precursors for these systems were synthesized by polycondensation reaction of XCl3 with bis(trimethylsilyl)carbodiimide or chemical modification of commercial polysilazanes with XY3(Y=H, Cl), then pyrolyzed at 823 to 1273 K under N2 or NH3. XRD, FT-IR and solid-state MAS NMR analysis were performed on the pyrolyzed samples. Hydrogen (H2) adsorption/desorption properties of the pyrolyzed samples were investigated by measuring H2 adsorption/desorption isotherms at 77 K and H2-TPD profiles after exposure to H2 at 423 K.

As our brief results, the polymer-derived X-ray amorphous AlCN and SiAlCN exhibited unique interactions toward H2 at low temperature of 77 K and over 423 K assigned to physisorption and chemisorption, respectively. The solid-state 27Al MAS NMR spectroscopic analysis for the AlCN and SiAlCN resulted in the detection of a particular short-range order with an unsaturated Al element.

The local structure around the unsaturated Al element could play an important role for the H2 physisorption followed by the chemisorption observed for the polymer-derived X-ray amorphous (Si)AlCN. At the poster session, the H2 adsorption/desorption properties characterized for the ternary XCN and quaternary SiXCN (X = Al, Ga) systems will be presented and discussed based on the results obtained by their local structure analysis and electrical properties.

Keywords: Hydrogen storage, Nitride ceramics, Group III-V ceramics

ABS 121

ENHANCED PERFORMANCE AND DURABILITY OF METAL-SUPPORTED FUEL CELLS BY OPTIMIZED CELL PROCESSING – RESULTS FROM THE CHRISTIAN DOPPLER LABORATORY

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Metal-supported solid oxide fuel cells (MSCs) are preferentially selected for mobile applications, e.g. as auxiliary power unit (APU) in heavy-duty trucks or as range extender for battery electric vehicles. The metallic support material allows the cells to withstand harsh operating conditions like fast thermal cycling, improves the mechanical stability and redox tolerance and offers novel possibilities for the internal reforming of hydrocarbons by catalytic activation. On the other hand the concept offers a potential for reducing the costs for cell production compared to established cell concepts and simplifies the sealing in a fuel cell stack by welding the substrate to the interconnects. The aim of this work was to enhance the Plansee MSC concept, in order to increase power density and avoid severe degradation of the cells.

To increase performance and long-term stability, new electrode materials, optimized processing routes for anode and cathode and tailored interfaces to the electrolyte and metallic substrate were investigated. Performance improvement was verified by electrochemical cell tests (I-V and EIS). Long-term tests at constant operation conditions enabled to study the durability of the cells. Degradation phenomena were characterized by oxidation test with subsequent microstructure investigations including SEM/EDX.

Replacing LSCF by LSC as cathode material in combination with optimization of particle size and sintering regime was found to clearly increase the electrochemical performance, especially at intermediate operation temperature in the range of 600 - 700 °C. For the fuel electrode, introduction of Ni/GDC instead of Ni/YSZ as the functional layer of the anode, accompanied by a stepwise optimization of the microstructure, resulted in another significant increase of cell performance. This effect was mainly based on enlarging the electrochemical active area. Furthermore, lowering the ohmic resistance across the cell by decreasing the electrolyte thickness was enabled by improving the anode surface quality. On the basis of these measures, cell performance could be enhanced from 0.12 A/cm^2 to 1.34 A/cm^2 at 0.9 V and 700 °C and long term stability was confirmed for up to 1500 h of operation without severe degradation. Moreover, MSC specific degradation phenomena caused by oxidation of the anode and metallic substrate, interdiffusion at the interfaces and Cr based poisoning of the cathodes were identified.

The presentation summarizes the main results achieved in the ´´Christian Doppler Laboratory for Interfaces in Metal-Supported Electrochemical Energy Converters`` since 2014 and generally discusses the potential for further increase of cell performance and long-term stability.

Keywords: Metal Supported Fuel Cell, High Performance, Optimized Processing

ABS 102

SOLID OXIDE ELECTROLYSIS CELLS - DEGRADATION PHENOMENA, ISSUES ADDRESSED AND FUTURE PROSPECTS

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Worldwide, interest has recently been focused on clean power generation in order to reduce emissions of CO2 and supply sustainable power. The intended shift from fossil resources to renewables requires new approaches for power generation and distribution, including energy conversion and storage. Solid oxide electrolysis cells (SOEC) are an attractive technology to convert surplus power to synthetic fuels such as H2 and CO/H2. However, specific degradation phenomena occur when operating solid oxide cells in electrolysis mode. This presentation reviews SOEC degradation modes and highlights approaches to overcome SOEC specific limitations.

Fuel electrode supported SOECs were fabricated at the Institute of Energy and Climate Research – Materials Synthesis and Processing (IEK-1) of Forschungszentrum Jülich. Similarly to solid oxide fuel cells (SOFC), the substrate is manufactured by tape casting the Ni/YSZ slurry, followed by screen printing of the fine grained Ni/YSZ functional fuel electrode layer. YSZ electrolyte, GDC diffusion barrier layer and LSCF air electrode are screen printed and sintered in subsequent steps. Cells of 5 x 5 cm^2 with 16 cm^2 active air electrode were tested in single cell measurements. Larger 10 x 10 cm^2 cells were assembled and tested for more than 18000 h in a two-layer stack setup. Post-test analysis was performed by SEM and EDX using embedded single cells and stacks.

Post-test analysis of the stack operated in SOEC mode for more than 18000 h revealed Ni depletion from the fuel electrode as the main cause of degradation, yielding a degradation rate of 8.2 %/kh. Impedance measurements indicate increase of the ohmic resistance to be more pronounced than electrode polarizations. Minor contributions to overall degradation were identified to result from demixing of the air electrode, zirconate formation and Cr poisoning.

Whereas degradation phenomena in SOFC operation are investigated in detail, giving a profound understanding of processes involved, SOEC specific degradation appears to be fundamentally different from observations in fuel cell mode. High vapor pressure of oxygen at the interface between electrolyte and electrode due to high current or insufficient oxygen ion conductivity of the electrode material is accepted to play a role in spallation of the air electrode. The most crucial aspect of fuel electrode degradation is Ni depletion from the functional layer. Here, the root cause is not yet clarified. Some explanations are based on evaporation of Ni(OH)2, which may be part of the process but is unlikely to be the main reason for loss of Ni.

Keywords: SOEC, Degradation, Ni depletion

ABS 101

TOWARDS HIGH-ENERGY SOLID-STATE LITHIUM BATTERIES WITH GARNET-TYPE ELECTROLYTES

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The application of garnet-type electrolyte thin films was studied, targeting at solid-state batteries with high energy density.

Firstly, the thermal/ chemical stability window $Li_5La_3(Zr,Ta)_2O_{12}$ with the so-called high voltage cathode active material $LiCoMnO_4$ was assessed in order to determine the temperature range for a successful combination. The materials showed different thermal stability for different compositions. Secondly, $Li_5La_3(Zr,Ta)_2O_{12}$ was deposited by a sputter deposition process as thin films.
A depletion of lithium in the sputter target can occur after several depositions, which leads to decreasing Li content in the electrolyte thin films. Therefore, the target was enriched with LiOH to compensate the lithium loss. Depositions carried out with a lithium rich target of $Li_5La_3Ta_2O_{12}$ showed the garnet structure on glass substrates after deposition at 500 °C, i.e. at significantly lower temperature compared to $Li_5La_3Zr_2O_{12}$. The garnet structure was observed on Au-coated EN 1.4767 substrates already at a substrate temperature of 400 °C, which is 300 K lower than comparable depositions of $Li_7La_3Zr_2O_{12}$.

While $Li_5La_3Zr_2O_{12}$ requires deposition temperatures of around 700 °C, $Li_5La_3Ta_2O_{12}$ needs deposition temperatures of 500 °C or even less for the cubic garnet phase, which is within the stability range of a combination of $Li_5La_3Ta_2O_{12}$ electrolytes and high-voltage spinels.

Keywords: solid-state lithium battery, garnet electrolyte, high voltage spinel cathode

ABS 90

POLYMER DERIVED SIOC CERAMICS AS A STRESS ACCOMMODATING NETWORK FOR IMPROVING THE ELECTROCHEMICAL STABILITY OF Sn ANODES IN Li-ION BATTERIES

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Lithium-ion batteries are widely used energy storage devices owing to their good electrochemical performance and lifetime. The electrochemical properties of the Li host electrode materials, however, have to be further developed in order to meet the requirements of high-performance future electronic applications. Among anode materials, Si and Sn have received much attention as an alternative to conventional carbon-based materials due to their remarkable electrochemical storage capacities. The practical application of these materials is still limited due to their low intrinsic electronic conductivity and volume expansion issues (e.g. up to 300% volume expansion for Si) leading to structural destruction during multiple lithiation/delithiation cycles. In the proposed work, carbon-rich SiOC ceramics will be investigated as a stress accommodating and conducting matrix to improve the electrochemical properties of Sn materials. Polymer derived SiOC ceramics have already gained a considerable interest as a potential anode material in the past two decades with the ability to deliver a capacity of more than 600 mAh/g. PDCs as a matrix can accommodate the volume expansion of Sn during high Li intake on one hand and on the other hand, it can also contribute some active Li storage sites thereby increasing the total storage capacity. The aim of this work is to elaborate an efficient synthesis route to investigate new host materials which could substitute conventional carbon-based anode materials for lithium-ion storage in commercial lithium-ion batteries. First-round electrochemical characterization of Sn/SiOC composite materials revealed reversible capacities above 700 mAh/g and Sn lithiation/delithiation activities were present even after 100 cycles of charging/discharging. Sn/SiOC materials also showed improved rate capabilities when cycled at high rates and showed an extended cycling stability of more than 200 cycles. With enhanced anode capacity and stability, the total battery capacity and cycling performance can be further improved.

Keywords: Polymer derived ceramics, Anodes, Li-ion batteries

ABS 88

PERFORMANCE OF THERMAL BARRIER COATINGS PRODUCED WITH AXIAL SUSPENSION PLASMA SPRAYING

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Suspension Plasma Spraying (SPS) is a flexible coating technology which allows under specific process conditions the manufacture of columnar structured coatings. This type of microstructure is very attractive for thermal barrier coating (TBC) applications as it result in a high strain tolerance. Recent results using the standard TBC material, yttria stabilized zirconia (YSZ), indicated that the specific stress state in combination with the mechanical properties of such coatings can lead to an early failure of these systems during severe thermal loading. In this presentation possible strategies to overcome this short coming by using double layer approaches will be presented and compared to results of coatings prepared by atmospheric plasma spraying (APS). In addition, results of multilayer Gd2Zr2O7 coatings with excellent performance under calcium-magnesium-alumino-silicate (CMAS) environment will be shown.

Keywords: thermal barrier coatings, suspension plasma spraying, CMAS resistance

ABS 64

SODIUM CONDUCTING SOLID ELECTROLYTE MEMBRANES BASED ON A GLASS CERAMIC MATERIAL

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Due to the opportunities to avoid the disadvantages of liquid electrolytes, lithium and sodium-based solid-state battery concepts move in the focus of applied research. Ceramic solid electrolytes provide improved safety, higher energy density and longer lifespan. Sodium as an ionic conductor in batteries has advantages over lithium such as availability and costs. The development of sodium based solid-state batteries using oxidic solid electrolytes is still behind established concepts like the ZEBRA or Na-S-Batteries which use high temperature sintering Beta-Al2O3 (> 1600°C) or NASICON (1250°C) with conductivities between 0,1 and 1 mS cm-1 at 25°C as solid electrolytes. These materials suffer from drawbacks like sodium evaporation and challenging manufacturing technologies. Glass based sodium conducting electrolytes can have sintering temperatures below 600°C but show low ionic conductivity. A solution that can compensate for the drawbacks of ceramics and glasses is given by glass ceramics in the Na2O-Y2O3-SiO2-system. It has been shown that well ion conducting glass ceramics (6.6x10-2 S/cm at 300°C) can be achieved by crystallizing of bulk glass specimens. This study demonstrates the ability of this material to be processed by ceramic technologies suitable for mass production as dense membranes via the powder route while keeping the required sintering temperatures below 1000°C.

Parent material compositions with additives were molten as a glass frit in a Pt-crucible and further processed as grinded powder. For the preparation of glass ceramic specimens powder compacts as well as casted tapes have been sintered and crystallized. The characterization of the material has been performed in terms of sintering behavior, phase formation, microstructure, mechanical properties and ionic conductivity by impedance spectroscopy.

It has been demonstrated that glass ceramics in Na2O-Y2O3-SiO2-system can be processed as powders by ceramic technologies such as pressing and tape casting. Optimized powder processing and sintering parameters lead to dense microstructures with a percolating conductive phase. Powder compacts achieve a bending strength up to 60 MPa and tape casted substrates (thickness <100µm) up to 160 MPa. In terms of ionic conductivity the glass ceramic material can compete with Beta-Al2O3 and also NASCION by achieving a conductivity of 0,5x10-3 S cm-1 at room temperature. The processing temperatures can be kept below 1000°C, which minimizes the formation of secondary phases and evaporation of sodium. Sodium conducting glass ceramic membranes can be synthesized by tape casting by taking the advantageous low sintering temperatures of a glass and preserving the well conducting properties of a ceramic material.

Keywords: Sodium, glass ceramics, solid electrolyte

ABS 46

NEW CATHODE MATERIAL OF NIOBIUM-DOPED LiCoPO$_4$ FOR Li-BASED BATTERIES

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Research of new materials with high electrochemical performance and thermal stability is a great challenge to develop Li-based batteries1. Amongst different materials used as cathode in Li-based batteries, the olivine-phosphate structures as LiMPO4 (M = Fe, Co, Ni, Mn) have been attracted large interest due high redox potential vs Li/Li+, good thermal stability and high theoretical capacity1. Although these materials are attractive due their high energy and power density, the main drawback is poor cyclability and low electronic conductivity, which depletes battery performance2. Different strategies have been used to improve electrochemical performance of the LiMPO4 cathodes, such as ionic doping, surface modification, particle size reduction and morphology control2. In this way, we prepared a new cathode material based on Niobium (Nb)-doped LiCoPO4.

The Nb-doped LiCoPO4 were prepared by solid state reaction, using stoichiometric amounts of Li2CO3, Co(NO3)2.6H2O, NH4H2PO4 and Nb2O5. All precursors were mixed in a high energy ball milling, at rotating speed of 300 rpm for 100 min. Powders obtained were heat-treated in a muffle at 900 °C (1h), with two heating level, at 650 °C (3h) and 350 °C (1h). The LiNbxCo1-xPO4 (x = 0, 0.01 e 0.05) were characterized by X-ray powder diffraction (XRD), Raman spectroscopy and Energy Dispersive X-Rays Fluorescence (EDXRF). The high densification pellets were obtained by innovative Spark Plasma Sintering (SPS) technique at 850 °C (10 min) with heating level at 450 °C for (10min), at 60 MPa. Electrical conductivity of LiNbxCo1-xPO4 pellets were evaluated by Electrochemical Impedance Spectroscopic using a two probe cell.

Our preliminary studies show that the LiNbxCo1-xPO4 has a orthorhombic olivine phase with Pnma space group (ICCD N° 01-078-5576). The Raman spectra indicated the presence of characteristic bands of the olivine structure in all samples, however the LiNbxCo1-xPO4 (x=0.01, 0.05) display a band around 870 and 670 cm-1 that could be attributed to the Nb incorporation in the LiCoPO4. Also, the EDXRF analysis corroborate the Raman studies, indicating that the Nb is in fact in the material. The EIS results suggest that the Nb could improve the total conductivity of the LiNbxCo1-xPO4 in comparison of the LiCoPO4 pure.

In conclusion, a facile and fast strategy has been developed to obtain a new cathode material based on Nb-doped LiCoPO4. The preliminary studies suggest that the LiNbxCo1-xPO4 has potential features to develop high-performance cathode materials for used in Li-based batteries for new generation.

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Keywords: niobium doping,LiCoPO4,all-solid-state battery

ABS 45

ENHANCING PHOTOCATALYTIC HYDROGEN EVOLUTION PERFORMANCE USING MoS_2/GRAPHENE HYBRIDS

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A MoS2-graphene hybrid (MSG) was synthesized by microwave assisted solvothermal method. Graphene modified MoS2 could tune the charge transfer resistance and the photo current as well. The charge transfer resistance decreased from 36,000 Ohm to 8.49 Ohm. The photo current could be enhanced from 0.29 mA cm–2 to 16.47 mA cm–2. Graphene has been reported to be an efficient cocatalyst for photocatalytic reactions because of its high specific surface area and good electron transfer abilities. In this article, the result has revealed that the appropriate modification of graphene could reach the maximum hydrogen yield. In addition, the appropriate conditions, such as the concentration of 0.318 M formic acid, and the MSG0.8 photocatalyst dose of 0.013 g L–1, could perform the excellent photocatalytic activity. In addition, the hydrogen evolution using MSG0.8 composite photocatalyst had the maximum yield of 667.2 µmol/h-gram.

Keywords: MoS2,Graphene Oxide, Photocatalytic Reaction

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CO-SINTERED CERAMIC CATHODES FOR ALL-SOLID-STATE BATTERIES

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Objectives Li-ion conducting ceramics are promising candidates for the use as solid electrolytes in future All-Solid-State, Li-Sulfur and Li-Air batteries. Especially all solid-state batteries exhibit significant benefits in gravimetric and volumetric energy density, operating temperature range and safety in comparison to conventional liquid electrolyte based systems. Full inorganic solid-state batteries based on amorphous or ceramic solid electrolytes, contain no flammable components and exhibit a high mechanical stability, making them less sensitive to damages. Various types of inorganic solid electrolytes with promising Lithium-ion conductivities have been developed and studied in great detail for use as ion conducting separators in the formerly mentioned battery concepts. However, the concept of full inorganic composite electrodes, including active material, electron conductive additives and a ceramic solid electrolyte, has been proposed for all solid state batteries but not yet investigated in detail or realized. This complex battery component requires a fundamental understanding of chemical and mechanical interactions among the components, which is rare in literature to date. Therefore, investigations on the development of composite electrodes based on typical cathode materials in combination with solid electrolytes are carried out.

Materials & Methods For the composite cathode, the NCM622 (LiNi0.6Mn0.2Co0.2O2) was co-sintered with the solid electrolyte LATP (Li1.3Al0.3Ti1.7(PO4)3) prepared by different synthesis methods. The compatibility of the active material with the solid electrolyte is studied by high temperature X-ray diffraction for different sintering temperatures. Furthermore, the microstructure of the sintered composites is analyzed. The co-sintered composite cathode is characterized electrochemically using a polymer electrolyte.

Results The X-ray diffraction indicates the reaction between LATP and NCM at a temperature of about 600 °C. Lithium phosphate and less complex oxides are detected as reaction products. Because of the formation of high resistant reaction products the sintering temperature should be decreased below 600 °C. The electrochemical performance is compared for samples with different properties due to the co-sintering process and discussed in detail.

Conclusions These experiments facilitated the understanding of reactions between the solid electrolyte and active materials at different sintering temperatures in order to evaluate suitable parameters for the processing of components for ceramic all-solid-state batteries. The first LATP-based composite cathodes have been prepared with adapted process parameters and demonstrate electrochemical functionality.

Keywords: solid electrolyte, Li all solid state batteries, co-sintered composite cathode

ABS 36

THE EFFECTS OF RARE EARTH DOPING ON THERMOELECTRIC PROPERTIES OF $NaCo_2O_4$

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Due to limited energy sources and environmental considerations, waste heat recovery is being essentially important and popular research field. Thermoelectric materials and devices are considered a promising possibility to convert energy between heat and electricity without moving parts or the release of greenhouse gases. However, because of low efficiency, relatively high cost and material toxicity thermoelectric devices are not commonly used. Recently, the NaCo2O4 system has attracted attention in thermoelectric application due to relatively high thermal stability, efficiency and lack of toxicity. In the present study, the effects of rare earth dopants (Yt, La and Ce) on the thermoelectric properties of NaCo2O4 has been systematically investigated. Pechini-based wet chemistry technique has been used for the sample preparation. The effect of calcination and sintering temperature on thermoelectric properties were examined. Rare-earth solubility in NaCo2O4 has been investigated and an isothermal section in the Na2O-CoO-La2O3 quasi-ternary system has been constructed. Additionally, structural, microstructural and electrical characterization of the rare-earth containing solid solution were performed. A systematic increment on the Seebeck coefficient was observed by the addition of ceria.

Keywords: Cobaltites, Metal oxides, Rare-earth doping

ABS 20

DEVELOPMENT AND CHARACTERIZATION OF Co- AND Mo-DOPED $SrFeO_{3-\delta}$ PEROVSKITES FOR REVERSIBLE SOLID OXIDE CELLS

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Currently, one of the most important challenges for the commercialization of reversible solid oxide fuel cell- electrolyser systems (SOFC-SOEC) is the optimization of the electrochemical properties of the air electrode at intermediate temperatures (500 -700 oC). Many perovskite (ABO3) materials are being developed as air electrodes due to their high ionic and electronic conductivities and good electrochemical activity. In this regard, SrFeO3-δ and SrCoO3-δ based compositions have been heralded as interesting air-electrode candidates because of their high electrocatalytic activity towards the oxygen oxidation-reduction. Although they suffer structural instability at high temperatures which lowers the oxide-ionic and electronic conductivities, recent studies have confirmed that doping in the B position improves the phase stability and the total electrical conductivity.

In this work, the effects of Mo and Co doping in SrFeO3-δ synthesized by a citrate/nitrate method have been studied for application as air electrodes in reversible SOFC-SOEC. The direct current four-probe method was used to study the electrical conductivity in air, O2 and N2 atmospheres of dense rectangular bars, whereas the ionic conductivity in air was evaluated by Faradaic efficiency using dense cylindrical pellets. The polarisation behaviour of the porous electrode material deposited on an electrolyte of Ce0.9Gd0.1O2-δ doped with 2 mol percent Co (10CGO-2 percent Co) was analyzed by impedance spectroscopy in air using a three-probe configuration. The oxygen reduction and oxygen evolution reactions of the materials in both configurations (SOFC and SOEC) were analysed by impedance spectroscopy under direct current fluxes. Co- and Mo-doping improves both the electronic and ionic conductivities of SrFeO3-δ due to a higher oxygen content and greater stability of the doped compositions. The electrochemical performance is also enhanced in the Co- and Mo-doped phases, which is associated with the effect of improved mixed-transport properties on the catalytic activity. Interestingly, the studied series exhibits better electrochemical behaviour for oxygen evolution in comparison to oxygen reduction, which suggests an improved performance as anode in SOEC in comparison to a cathode in SOFC, and highlights its potential as air electrode in reversible systems.

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Keywords: Reversible solid oxide cell, Perovskites, Co- and Mo-doped SrFeO3

ABS 19

OPTIMIZATION OF $Ce_{0.8}Gd_{0.2}O_{1.9}$-$FeCo_2O_4$ DUAL PHASE MEMBRANES WITH VARYING HOMOGENEITY AND GRAIN SIZE OF $FeCo_2O_4$

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Dual phase membranes (DPM) possess good chemical stability for long term operation with application relevant oxygen permeation. Microstructural aspects like homogeneity and grain sizes, in particular also of the minor phase, can strongly affect membrane properties. However, no study has been reported on microstructural adjustment and optimization of an individual phase. Hence, the goal of the current study is to tailor homogeneity and grain size of the minor phase in DPM while retaining grain size of the matrix phase. The relationship between microstructural variation of the minor phase and properties will be discussed based on experimental evidence.

The main focus is on 85 wt% Ce0.8Gd0.2O2-δ-FeCo2O4 (CGO-FCO) dual phase membranes sintered at 1200 °C for 10 h through beneficial phase reaction of powder mixtures of Ce0.8Gd0.2O2-δ, Co3O4 and Fe2O3. Powder milling processes differ by using 5 and 1 mm ZrO2 balls separately with different milling times ranging from 1 to 10 days.

The XRD patterns confirmed the phase structures of fluorite and spinel, as well as a newly formed perovskite phase through the reaction of both. The SEM investigations revealed a similar average grain size of around 0.7 µm for CGO grains in all samples, but the spinel grain sizes varied in case of the altered powder milling processes. The powders milled by 5 mm balls for 1 and 3 days reveal agglomeration of Co3O4 and Fe2O3 particles, resulting in large spinel grains with an average size of around 1.2 µm after sintering. Also detected are several microcracks, which might be induced upon cooling by a thermal expansion mismatch between the phases. Whereas, 7 and 10-day milling with 1 mm balls generates more homogenous powder mixtures, resulting in microcrack-free microstructures with smaller spinel grains of around 0.3 µm. Meanwhile, the average flexural strength of samples prepared from long-time milled powders is significantly improved to around 241 MPa, which is nearly double the value (around 132 MPa) of samples prepared from short-time milled powders, while there is no significant difference of elastic moduli. In addition, the possible influence on the oxygen permeation rate is subject of current investigations.

The results indicate that a crack-free and homogeneous microstructure of DPM with reduced grain size of the minor phase, improved flexural strength drastically and possibly enhanced O2 permeation can be obtained via a longer milling process with small milling balls, while the grain size of the matrix remains almost in the same range.

Keywords: dual phase membranes, homogeneity, grain size

ABS 3

CHARACTERISATION OF SOFC-DEDICATED GLASS-CERAMIC SEALS COMPOSED WITH THE USE OF RECYCLED MATERIALS

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Solid oxide fuel cell technology is considered as very promising future way for small or medium scale green energy generation because of very high efficiency and no harmful gas emissions. One of the research areas concerning this technology is material aspects of reliable seals that withstand high temperature of SOFC continuous long-term operation (600-800°C) and provide a gas-tight barrier between hydrogen and air compartments of the stack. A known commercial solution dedicated for SOFC stack designers is glass powder of thermal expansion coefficient matching the value of sealed elements, which is classified as a rigid type of seal bonding the elements permanently after the glass is softened in certain temperature. The drawback of this solution is low mechanical strength, possibility of application only as very thin layers and high compression rates of the seals, which is difficult to implement in the stack design. Some drawbacks can be overcome with the use of hybrid seals, where the glass layers are laminated with mica sheets or other materials, however, it complicates the technology and overall cost is high, which hinders the industry from producing SOFC-based power generators on large scale.

The aim of the research was to study the characteristics of SOFC-dedicated composite seals that are based on commercial glass powder and have recycled materials as infill, such as stabilized zirconia waste, mica flakes or residuals from fabrication of similar glass-mica gaskets. Addition of recycled materials lowers the manufacturing costs, changing the compression profile during sealing, which could simplify the implementation of the seals in SOFC stack designs. Sample gaskets composed with the use of various recycled materials were fabricated by tape casting and tested in SOFC stack operating conditions regarding temperature and load pressure. The specially designed test bench allowed to measure compression profile during sealing procedure as well as gas-tightness of the seal at high temperatures under pressure drops, similar to operation mode of the SOFC. Thermocycling studies, performed from cold restart, demonstrated that gaskets can keep their sealing properties if compressive force was not reduced.

Keywords: SOFC, seal, glass-ceramic seal

S07

FUNCTIONAL CERAMICS

INVITED LECTURES

ABS 847

MULTIFERROIC CERAMIC MATERIALS FOR ROOM TEMPERATURE MAGNETOELECTRICITY: RECENT ADVANCES IN SINGLE-PHASE AND COMPOSITE APPROACHES

M. ALGUERÓ [1], H. Amorín [1], C.M. Fernández-Posada [1], J.A. Quintana-Cilleruelo [1], P. Ramos [2], R. Moreno [3], W. Santa-Rosa [4], M. Venet [4], A. Castro [1]

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The solid state linear magnetoelectric effect is the development of an electric polarization proportional to an applied magnetic field, and conversely of a magnetization in response to an electric field. Magnetoelectrics are a key enabling material technology for a range of potentially disruptive related ones, such as electrically-tunable magnetic-microwave or spintronic devices, high-sensitivity magnetic sensors with room-temperature operation, and microgenerators for wireless sensor networks or bioimplanted systems.

A main line of research is single phase multiferroics, as these compounds can show large magnetoelectric effects and coupled ferroelectric and magnetic domains. This opens the way for achieving the reversal of magnetization with an electric field and thus, for developing electrically-writable, magnetically-readable non-volatile random access memories. However, large magnetoelectric effects have only been obtained at very low temperature, and a functional material capable of enabling the proposed technologies has not been found. In the first part of the talk, most promising single phase approaches for room temperature magnetoelectricity will be briefly highlighted. Specifically, recent work on perovskite systems chemically engineered to be placed at instabilities of the multiferroic state for phase-change magnetoelectric response will be reviewed [1].

Alternatively, magnetoelectric coupling can be achieved by composite approaches. Rationale is to combine ferroelectric and ferromagnetic phases, so that magnetoelectricity is obtained from their electrostatic, magnetic or elastic interaction. The largest effective room-temperature magnetoelectric coefficients have been obtained for composites consisting of elastically-coupled high-sensitivity piezoelectric and magnetostrictive phases. Among composite approaches, cofired ceramic layered structures offer improved reliability in applications and are more adequate for mass production and miniaturization. In the second part of the talk, open issues relating their processing and functional response will be discussed. Concretely, latest work on the fabrication of multilayer ceramic composites by tape casting technology, combined with spark plasma sintering, and on the geometric parameters affecting functionality will be also reviewed and updated [2].

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Keywords: Magnetoelectrics, Single-Phase, Composites

ABS 842

STRUCTURAL DESIGNS FOR FERROELECTRIC CERAMICS AND APPLICATIONS IN FUTURE ELECTRONICS

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Structural designs are important to generate novel functions of electronic ceramics. A typical example of these structural designs is a multi-layer ceramic capacitor (MLCC). It has hierarchical structures, i.e. core - shell structure, grain - grain boundary structure, ceramic - electrode monolithic structure, and so on. Each structure should be designed to optimize the performances of the MLCCs.

Another examples of the structure designs for novel functions are piezoelectric ceramic devices. A precise device structure for some lead-free piezoelectric ceramics such as multi-layer structures leads to comparable piezoelectric properties with lead containing ones. Moreover, precise layer structures of piezoelectric bodies control their elastic wave propagations, and realize suitable resonance characteristics for electronic devices.

Thus, in various electronic ceramic applications, structural designs have played key roles to exhibit high performances. Other examples such as thermistors, thermoelectric devices, are also taken, and the importance of the structural designs of ceramics for advanced electronic devices is emphasized with these examples.

Keywords: piezoelectric, Multi layer ceramic capacitor, structural control

ABS 786

MANUFACTURING PROCESSES OF RARE-EARTH OXIDES TRANSPARENT CERAMICS FOR HIGH POWER LASER APPLICATIONS

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Transparent ceramics of rare-earth oxide family are well adapted to manufacture optical components of high power lasers. In fact, oxides of garnet (e.g. Y3Al5O12 - YAG) and sesquioxide (e.g. Lu2O3) families are very interesting as they present good thermomechanical properties and because they can be heavily doped with luminescent dopants (Nd3+, Yb3+, Ho3+, etc.) [1,3]. Moreover, the flexibility of ceramic processes allow manufacturing of pieces with various shape and/or concentration gradient that can improve the final laser system performances. The objective of this study is to develop an integrated approach of transparent ceramic processes with a deep understanding of the influence of each key parameters of the process.

This work is focused on shaping and sintering of rare-earth oxide transparent ceramics. First, liquid way shaping processes of colloidal suspensions like pressure casting and tape-casting were developed. Various characterizations were lead in order to control suspensions properties that must be adapted to the process. In addition, green compacts characteristics, especially microstructure homogeneity and concentration gradient, were investigated. This work show that liquid-way shaping processes are well adapted to manufacture transparent ceramics with concentration gradient. Various architectures (segmented with longitudinal or radial gradient, continuous gradient, waveguide, etc.) were obtained by pressure casting and tape-casting. Also, these processes allow to obtain transparent ceramics with near to theoretical optical transmittance after sintering. They promote a homogeneous microstructure in green compacts with very narrow pore size distribution that can be totally removed during sintering.

Finally, conventional (pressureless sintering) and non-conventional sintering techniques like post-HIP (Hot Isostatic Pressing) or SPS (Spark Plasma Sintering) were investigated. Sintering maps were used to understand the evolution of materials microstructure during sintering. Their analysis lead to a better understanding of porosity evolution and elimination during the thermal treatment. As a result, using of pressure-assisted sintering techniques appears very efficient to promote densification with limited grain growth. Finally, highly transparent ceramics of various composition and architecture with improved thermomechanical properties were manufactured (Figure 1: Transparent ceramics of Nd3+:YAG with homogeneous doping (a) with concentration gradient (e), Ho3+:YAG (b), Cr4+:YAG (c), Nd3+:Lu2O3 (d))

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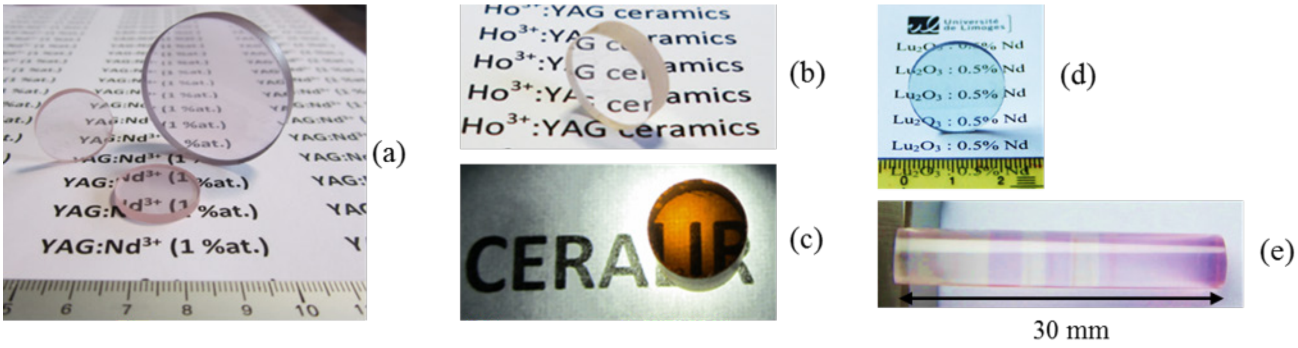
Keywords: YAG, Lu2O3,Tape-casting,Hot Isostatic Pressing



ABS 558

FUNCTIONAL ELECTROCERAMICS: THE COMPLEX STRUCTURE BEHIND SIMPLE CURVES

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Functional electroceramics are used in a broad range of applications such as electromechanical devices, microelectronics, heating or cooling elements as well as sensors and actuators. Highest functional properties can be observed in the vicinity of phase boundaries. Dielectric and piezoelectric coefficients peak towards these regions. Therefore, compositions of highest technological interest, in many cases, exhibit phase coexistences. These phases usually are highly correlated, complicating quantitative analysis. Additionally, uniaxial forces such as electric fields or mechanical stresses impose a preferred orientation. In the past years we developed a method that is able to describe all electromechanical effects that occur during operation of these materials. Based on crystallographic methods we are able to calculate the macroscopic behavior, such as electric field induced strain, on a model based on the atomic scale. When the strain is measured in abipolar way, these strain hystereses exhibit a rather clear and continuous behavior. However, the underlying structural and microstructural mechanisms can be quite complex. In this contribution the underlying mechanisms of relaxor and ferroelectric materials is elucidated on a structural and microstructural level.

Keywords: electric field, diffraction, strain

ABS 468

CATION ORDERING AND PHASE COMPETITION IN Ba8M2+M’5+6O24 HEXAGONAL PEROVSKITE TANTALATE AND NIOBATE DIELECTRICS

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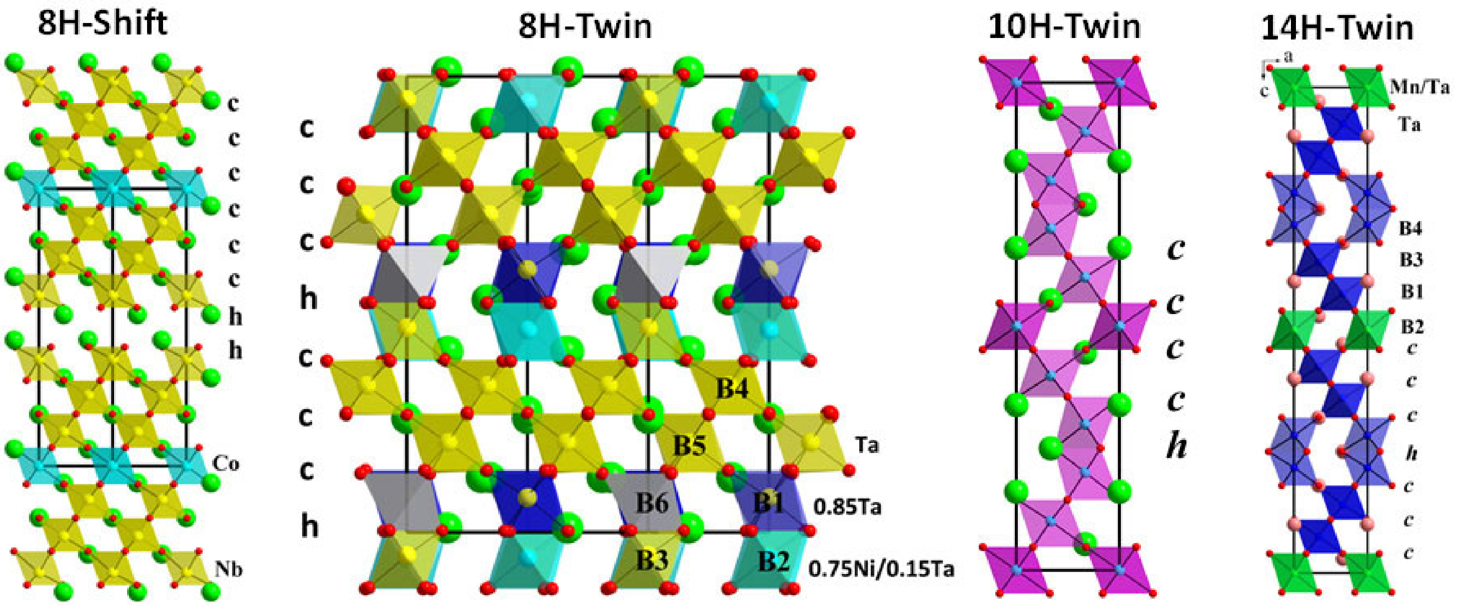
Ba8M2+M’5+6O24-type B-cation deficient hexagonal perovskite tantalates and niobates attract attention as microwave dielectric resonators because of their high quality factors and interesting structural chemistry. 8-layer hexagonal perovskite Niobates display twin-shift option and rarely nanometer-scale long-range cation order has been observed in the shifted Ba8CoNb6O24, Ba8ZnNb6O24 and Ba8MnNb6O24 so far. While their Ta-counterparts form exclusively twinned structures. Here we details the correlation of the cation order and phase competition with the B-cationic size and charge differences as well as the bonding preferences associated with the bonding covalence and the second-order Jahn-Teller (SOJT) effect of d0 Nb5+ and Ta5+ in the Ba8M2+M’5+6O24 hexagonal perovskites. Also we present the Ta5+-substitution effect on lowering the temperature coefficient of resonant frequency τf of 8-lyaer shifted hexagonal perovskite dielectrics toward near-zero τf values.

Keywords: Cation ordering, Phase competition, Hexagonal perovskite



ABS 439

(K,Na)NbO_3-BASED LEAD-FREE PIEZOCERAMICS: TOWARDS TEMPERATURE-INSENSITIVE HIGH PIEZOELECTRICITY

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Piezoelectric materials enable the conversion between mechanical and electrical energy and developing high-performance lead-free piezoelectric ceramics has been one of the most active materials research topics in the last decades. Despite the great progress, either lack of high piezoelectricity or insufficient thermal stability of piezoelectricity still hinders the actual applications of lead-free piezoelectric ceramics. In this work, we present a new high-performance potassium sodium niobate based lead-free piezoelectric ceramic with frequency-insensitive high piezoelectric strain coefficient (d33* above 600pm/V) in a wide temperature range, of which the overall performances are superior to the other representative lead-free piezoelectric ceramics and are comparable to the commercialized PZT-based ceramics. The electrical property measurement and nanostructure observation revealed that the high performance combining high piezoelectricity and excellent stability benefits from diffused phase transition, which is closely associated with the transition from ferroelectric to relaxor behavior induced from the local structural disorder due to the complicated compositional modification. The high-resolution transmission electron microscopy observation suggests the existence of polar nanoregions that are responsible for the relaxor-like electrical behavior in the present materials. The finding and understanding obtained in this work should be valuable for pushing lead-free piezoelectric ceramics towards practical applications.

Keywords: lead-free piezoelectric, niobate, ferroelectric

ABS 253

MICROWAVE CERAMICS FOR 5G AND BEYOND

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The data transmission rates as we move from 4G to 5G and beyond will increase dramatically from 100 MB to >1GB. To accommodate this increase, higher frequencies will be utilised (28 GHz) whose wavelengths are in the mm rather than cm range. The use of such frequencies is problematic with major issues relating to absorption of the MW signal by the atmosphere and urban environment and lower loss materials required with lower permittivity than those developed for 2 - 4G applications. The 5G materials road map includes, new low loss substrates for antennas, new resonator ceramics with lower loss and lower permittivity and steerable antennas to reduce the excessive power requirements to penetrate urban environments. New materials and new materials concepts will be discussed in light of the 5G revolution which have the potential to overcome current limitations in materials.

Keywords: 5G,ceramic,cold sintering

ABS 876

COMPLEX INTERACTIONS BETWEEN DOMAIN WALLS AND PINNING CENTERS: IMPLICATIONS TO PIEZOELECTRIC NONLINEARITY AND HYSTERESIS

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Displacements of domain walls under subswitching fields in ferroelectrics may account for a large, sometimes dominant fraction of the total macroscopic response and are largely responsible for the piezoelectric and dielectric nonlinearity and hysteresis. From a microscopic perspective, domain-wall displacements are usually linked to the medium in which they move, represented by pinning centers or charged point defects. A known example of a strong interaction between domain walls and defects can be found in hard ferroelectrics, such as acceptor-doped Pb(Zr,Ti)O3, where the pinning mechanism arises due to the presence of defect complexes associated with oxygen vacancies. Although well understood in Pb(Zr,Ti)O3, we will show by using the example of BiFeO3 that hardening mechanisms may be far more complex than usually assumed. Using chemical and structural analysis on the atomic scale, it will be shown that pinning effects in BiFeO3 are most likely dominated by electron-hole defects accumulated in domain-wall regions. This gives rise to a mechanism in which the electrical conductivity and domain-wall displacements become coupled, resulting macroscopically in large piezoelectric nonlinearity and hysteresis at low (Hz and sub-Hz) driving field frequencies.

Interactions between domain walls and defects represent only one among diverse mechanisms that may control domain-wall dynamics and thus macroscopic hysteresis and nonlinearity at subswitching fields. A class of materials in which this picture might be even more complex is relaxor-ferroelectrics, exemplified by Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT), where additional complexity arises from presumable presence of polar nanoregions, which may couple to the spontaneous polarization inside domains, and complicated hierarchical nanodomain structures. We explore these issue by analyzing in detail the piezoelectric and dielectric nonlinear response of PMN-xPT compositional series spanning from x=0 (pure PMN) to x=0.5. The data reveal a strongly nonlinear and hysteretic response in a broad range of compositions spanning the monoclinic phase region of the PMN-PT phase diagram. This response cannot be entirely described by Rayleigh-like interface dynamics and is different from what is believed to be the nonlinear contribution of polar nanoregions in the ergodic PMN. While the origin of this behavior is still not clear, we will tentatively discuss it based on the relaxor behavior in the PMN-xPT system as well as dynamics of domain walls in hierarchically structured monoclinic nanodomains.

Keywords: domain walls, defects, piezoelectric response

S07

FUNCTIONAL CERAMICS

ORAL PRESENTATIONS

ABS 851

EFFECT OF DIFFERENT PEROVSKITES ON THERMALLY-STABLE DIELECTRIC PROPERTIES OF BISMUTH FERRITE–BARIUM TITANATE CERAMICS

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Objectives The general objective of the current research work is to investigate thermally-stable dielectric properties of lead-free 0.65Bi1.05FeO3–0.35BaTiO3 ceramics modified by 3 mol% and 10 mol% BiGaO3 and (BiNa0.84K0.16)0.48Sr0.04TiO3 content, respectively, for the high temperature dielectrics.

Materials and Methods Different ceramic compositions, 3 mol% BiGaO3 (BG3) and 10 mol% (BiNa0.84K0.16)0.48Sr0.04TiO3 (BNKS10)-modified 0.65Bi1.05FeO3–0.35BaTiO3 (BF–BT) lead-free ceramics were prepared by a solid-state reaction method. The same synthesis route and all (structural, ferroelectric and dielectric) characterizations were achieved according to our previously published articles [1, 2].

Results The XRD patterns of BF–BT–BG3 and BF–BT–BNKS10 revealed a single perovskite crystal structure without any ostensible secondary phases. Noticeable variations in ferroelectric and thermally-stable dielectric properties were experiential by the addition of BG3 and BNKS10 in the host BF–BT dielectrics. The system exhibited temperature-stable εr (850–980), high Tmax (>400 oC), colossal εrmax (4428–46363), and εrmid (2286 to 2891±15%) across the wide temperature range. Thermally-stable high dielectric properties make this system suitable for high temperature dielectric applications.

Conclusion We report comparative analysis of microstructure, ferroelectric and thermally-stable dielectric properties of 0.03BiGaO3 and 0.10[(BiNa0.84K0.16)0.48Sr0.04TiO3]-modified 0.65Bi1.05FeO3–0.35BaTiO3 lead-free dielectrics (abbreviated as BF–BT–BG3, and BF–BT–BNKS10, respectively), which were synthesized by a solid state reaction route. The structural properties (XRD-patterns) of both modifiers hold a pure perovskite structure and a pseudocubic symmetry without any existence of secondary phase. The addition of BG3 and BNKS10 caused considerable variation in morphology in the base BF–BT materials. BNKS10-content results in a large degradation in remnant polarization (Prem) and coercive electric field (Ec) as compared to BG3-content in the host BF–BT dielectrics. Temperature dependent dielectric measurements exhibited ferroelectric-relaxor characteristics with dielectric mid-value permittivity εrmid~2286±15% in the temperature range from 198 °C to 332 °C for BF–BT–BG3 systems at 100 kHz of frequency. For the BF–BT–BNKS10 compositions the temperature range of stable dielectric permittivity extended to 244 °C–500 °C, with εrmid~2891±15% at the same frequency. These investigated results are favorable in the perspective of developing new eco-friendly high temperature dielectric applications.

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Keywords: Lead-Free, Ferroelectrics, Dielectrics

ABS 926

ENHANCED MAGNETIC PROPERTIES IN BULK CERAMIC NANOSTRUCTURED COBALT FERRITES

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Materials with hard magnetic properties are key components in a large number of relevant technological applications. For these applications ceramics represent a promising alternative to hard magnetic alloys, such as ALNICO and rare earth alloys, thanks to their low-toxicity, high chemical stability, high melting point, high abundance and low cost. However, ceramic hard magnets, such as ferrites, show magnetic properties that are significantly lower than in rare earth alloys. Nanostructure can, in principle, increase considerably these properties when single domain or strong correlation regimes are obtained. These effects have been extensively reported in nanopowders, but the synthesis of bulk materials, which preserve these characteristics, has received limited attention.

In this work bulk nanocrystalline cobalt ferrites have been obtained by sintering nanopowders with high pressure field assisted sintering (HP-FAST). The nanopowders are synthesized using various solution approaches and present a particle size of 20-30 nm and are then sintered at a temperature between 300 e 600°C and using a pressure up to 2 GPa reaching a final particle size of 40-50 nm. The variations of parameters in the sintering process produce a differentiation in the microstructure of the sintered samples. Completely uniform and homogeneous samples have been obtained imposing the sintering pressure before the beginning of the heating cycle. The relative density of the sintered samples varies in a range between 88 and 100%. The magnetic properties of the sintered materials have been measured with a physical property measurement system (PPMS) using a vibrating sample magnetometer (VSM). The differentiation in the microstructure leads to differences in the magnetic characteristics. It has been noticed that the samples with the best hard magnetic properties are characterized by microstructures that are not completely homogeneous.

Sintered samples presenting ferromagnetic behavior at room temperature with a coercivity from 1000 to 2000 Oe, a saturation magnetization of 50-70 emu·g-1, and a remanent magnetization between 18 and 39 emu·g-1 have been obtained. These are confrontable with the values typical of cobalt ferrites nanoparticles.

Keywords: Nanostructure, Hard ferrimagnets, Oxides

ABS 800

MULTI-PHASE FIELD FORMULATION FOR FERROELECTRICS NEAR THE POLYMORPHIC PHASE BOUNDARY: INSIGHTS INTO BZT-BCT

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Lead toxicity has motivated the search for Pb-free ferroelectrics to replace PZT, whose optimal properties near its interferroelectric transition are associated with a reduction of the crystallographic anisotropy of the free energy. For systems with interferroelectric transitions that are driven by temperature, i.e. possess a polymorphic phase boundary (PPB), similar principles are expected to hold. Existing modelling methodologies artificially couple the free energies of the bulk ferroelectric phases with different symmetries. Thus, the PPB and structural states in ceramics near this region of phase space are not able to be examined.

Here a novel phase-field approach is proposed to describe PPB ferroelectrics. The formulation allows the properties of the two ferroelectric phases to vary independently. Model parameters are fitted to experimental data from BZT-40BCT ceramics. This composition is tetragonal (T) at high temperatures and rhombohedral (R) at low temperatures. There is debate about whether this system has a single PPB with a region of R+T coexistence near the PPB temperature or whether there is an intervening orthorhombic (O) phase instead. Our predictions for BZT-40BCT are consistent with experimental observations of a R+T coexistence region. A maximum temperature for coexistence is predicted from thermodynamic analysis and agrees with the experimentally observed upper transition temperature. The time-temperature-transformation behaviour indicates that low temperature coexistence is kinetically limited.

This method can be used to validate competing theories regarding the enhanced properties near the PPB in the search for Pb-free materials.

Keywords: phase-field modelling, ferroelectric TTT relations, stability analysis

ABS 921

ELECTRO-MECHANICAL COUPLING IN YSZ DUE TO REORIENTATION OF CATION-OXYGEN VACANCY CLUSTERS

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It is well established by now that doping of ZrO2 with aliovalent cations, not only stabilizes the high-temperature cubic structure of ZrO2 down to the room temperature, but also introduces additional vacancies on the oxygen sublattice and thus enhance their ionic conductivity. Cubic ZrO2 doped with 8 mol% Y2O3 (8YSZ) has been one of the most commonly used solid state ionics in various applications such as solid oxide fuel cells (SOFCs) and oxygen sensors. Oxygen vacancies formed as a result of doping with Y2O3 can freely move at high temperatures (above 600 °C) leading to the high ionic conductivity of the material. However, at low temperatures (below 600 °C), oxygen vacancies are trapped by immobile opposite charged cations even in dilute solutions in cation-oxygen vacancy clusters. Those clusters are electric and elastic dipoles and when the material is heated at temperatures above 100 °C, oxygen vacancy can hop to another position around the dopant cation to change the dipole orientation under applied electric field or mechanical stress. We have shown that starting from that temperature it is possible to record electric field-polarization hysteresis loops due to reorientation of cation-oxygen vacancy dipoles. Since the crystal lattice deformation depends on dipoles orientation and vice versa it is possible to change hysteresis shape and size by application of mechanical stress in direction parallel to electric field. At temperature above 500 °C diffusion processes and thermal vibrations are so pronounced that interactions between cation and oxygen vacancies are too weak to hold them together, i.e. dipoles dissociate and 8YSZ becomes conductive. The existance of dipoles that could be reoriented in temperature interval from 100 to 500 °C has been also proved in this study by piezo measurements. Sinusoidal mechanical stress induced sinusoidal electric response and piezoelectric parameter g33 was calculated. Parameter g33 is both temperature and frequency dependent and increases with increase in temperatue and frequency. At temperature of 330 °C and frequency of 10 Hz value of g33 of the 8YSZ was 5.08 · 10^(-8) Vm/N. Unlike to ferroelectric materials in which piezoelectric coupling is related to domain switching, the observed effect in 8YSZ is related to the reorientation of electric dipoles under applied stress and electric field.

Keywords: YSZ, electro-mecanical coupling, cation-oxygen vacancy dipole

ABS 776

ROLE OF ZnO-DOPANT IN SINTERING AND ELECTROMECHANICAL PROPERTIES OF HIGH COERCIVE FIELD LEAD ZINC NIOBATE BASED PIEZOELECTRICS

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A major limitation of many high power relaxor-based ferroelectric materials is their maximum operating temperature. The Pb(In1/2Nb1/2)O3-Pb(Zn1/3Nb2/3)O3-PbTiO3 (PIN-PZN-PT) perovskite solid solution possesses a high rhombohedral to tetragonal phase transition temperature (Tr-t) and Curie temperature (Tc), while also having a large piezoelectric charge coefficient (d33), coercive field (Ec), and mechanical quality factor (Qm). While ZnO-doping is required to stabilize the perovskite phase, the role of the ZnO on sintering and electromechanical properties has not been explored. This work explores the relationship between ZnO doping and defect chemistry on the densification and piezoelectricity of PIN-PZN-PT ceramics. ZnO doping resulted in the formation of a liquid phase that assisted in densification. The incorporation of zinc ions into the perovskite lattice increased the tetragonal character of the perovskite. Sintering atmosphere has a dramatic effect and will be reported.

Keywords: Piezoelectric, Ferroelectric, High Power

ABS 772

THE INFLUENCE OF POLAR ORDER ON THE PHOTOLUMINESCENCE OF Eu:$BaZr_xTi_{1-x}O_3$ CERAMICS

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The ability to tune and enhance the properties of photoluminescent materials (phosphors) is essential for optimizing the performance of devices and understanding the luminescence mechanisms. The trivalent europium ion (Eu3+) is well known for its strong luminescence in the red spectral region. Even a very small variation in the coordination sphere of europium ions induces major changes in the emission spectrum. Therefore, Eu3+ was used as a local structural probe for studying the impact of ferroelectric order and, more generally, of polar order on the photoluminescence emission. The BaZrxTi1-xO3 solid solution was selected as a model host structure as it exhibits a progressive evolution of the polar order, from long-range order typical of classic ferroelectrics (x = 0-0.15), via a diffuse transition behaviour (x = 0.15-0.25), to short-range order typical of relaxors (x >= 0.25) until the paraelectric non-polar state of neat BaZrO3 is achieved.

The photoluminescence emission of dense BaZrxTi1-xO3 ceramics (x =0.0, 0.05, 0.15, 0.30, 0.50, 0.70, 1.0) doped with 1 at.% Eu3+ at the Ba site was investigated in the temperature range -100 to 140°C. The dielectric permittivity of the samples was measured from -150 to 150 °C at 100Hz-1MHz Hz to determine reference values of the phase transition temperatures and the type of polar order. The PL spectra underwent significant shape and intensity variations as a function of both composition and temperature. Ferroelectric ceramics show an abrupt inversion of the relative intensity of the dominant Eu3+ emission bands with temperature, determined by the displacement of the lanthanide from the dodecahedral Oh site of Ba2+ to a slightly distorted D4d site. The off-centering is attributed to the cooperative polar interactions in the ferroelectric lattice, i.e. the correlated displacement of Ti4+ and Eu3+ ions. Despite the larger unit cell, Eu3+ mainly occupies the centrosymmetric Ba2+ position in BaZrO3 due to the absence of polar order leading to a nearly temperature independent luminescence spectrum. Relaxors show a more complex emission behavior determined, at least in part, by their intrinsic heterogeneous nature at the nanoscale.

Keywords: Photoluminescence, Ferroelectrics, BaTiO3

ABS 918

CRYSTAL CHEMISTRY AND MAGNETISM OF IRON-TUNGSTEN MIXED OXIDE

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Iron tungstate Fe2WO6 attracts interest due to its photoelectrochemical and magnetic properties. On the one hand, Fe2WO6 is studied either as a photocatalyst for degradation of environmental pollutants [1,2] or as a photoanode for water oxidation in tandem devices [3-4]. On the other hand, some magneto-dielectric properties [5] have been reported, confirming that further work is needed to investigate the magnetic and electric properties. Indeed, Fe2WO6 iron tungstate exists as three crystal structures with different organizations of the FeO6 and WO6 octahedra [6-8].

In the present work, we have clarified the conditions of polymorphism using a complete set of the three polymorphs as single-phase products. In particular, a spray-drying route from aqueous solution had to be developed for the synthesis of the low temperature α-polymorph. We have revised the structural model for this α-polymorph, solved the heretofore-unknown structure of the β-polymorph and compared magnetic properties through bulk magnetic measurements and preliminary neutron diffraction results. We also report on the influence of the Fe/W ratio using a combination of X-Ray diffraction, 57Fe Mossbauer spectroscopy, scanning electron microscopy and ICP-OES quantification.

The kindly acknowledge F. Fauth, beamline responsible (BL04-MSPD) at ALBA synchrotron, for his help.

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Keywords: polymorphism, magnetic properties, spray-drying

ABS 670

DEVELOPMENT OF HIGH TEMPERATURE SURFACE ACOUSTIC WAVE SENSORS BASED ON A PIEZOELECTRIC GLASS-CERAMIC

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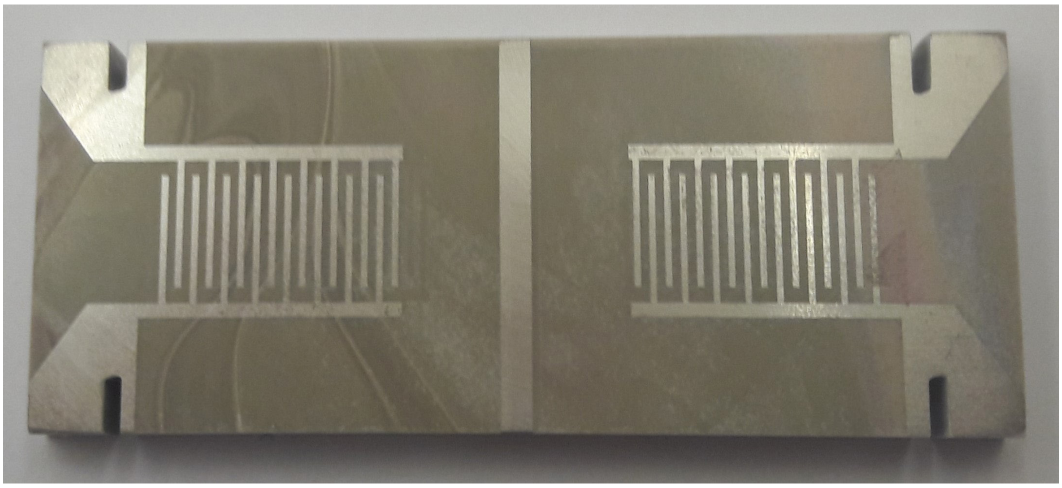
This work is part of a project aiming at developing high temperature pressure sensors using surface acoustic waves (SAW). To this end, a non-ferroelectric piezoelectric glass-ceramic containing fresnoite crystals is evaluated to be used as substrate for the interdigitated electrodes (IDT). The ability of this glass-ceramic to work up to 800°C is evaluated.
A parent glass plate is obtained by mixing reagent-grade SrCO3, TiO2, SiO2, K2CO3 and Al2O3, melting the mixture at 1500°C, and then casting the molten glass. This glass is crystallized at 900°C in a powder bed to induce surface crystallization, leading to a piezoelectric glass-ceramic. Glass transition temperature Tg is estimated by thermal expansion technique. The crystal structure is characterized in temperature by HT-XRD. Young's modulus and damping are measured by high temperature IET. A testing device composed of two platinum IDT (emitter and receiver), deposited on a glass-ceramic substrate is realized to evaluate the ability of the material to generate and propagate SAW in temperature. A fresnoite glass-ceramic was successfully synthesized through isothermal heat treatment of a glass. To obtained material is composed of 70 vol% Sr2TiSi2O8 crystals and 30 vol% residual glass. The crystals are preferentially oriented over a depth sufficient to generate and propagate SAW. It is proven by HT-XRD that the crystal structure is stable up to 1000°C. Dilatometry measurements show that the glass transition temperature of the residual glass is around 650°C. Above this specific temperature, the IET measurements show a decreasing elastic modulus and an increasing damping. These phenomena become more drastic above 800°C. The evolution of relative amplitude of the SAW collected on the receiving IDT over temperature can be divided in 3 parts. First, there is a slow decrease from RT to Tg, probably due to the thermal expansion mismatch between the crystal and the glassy phase leading to stress and microcracks. Then, the amplitude strongly increases from Tg to 800°C, as the piezoelectric crystals are less constrained by the residual glass which is becoming viscoplastic. Finally, the amplitude drastically falls above 800°C because of a high damping due to the residual glass low viscosity. A SAW device based on a piezoelectric non-ferroelectric glass-ceramic was developed, and its ability to generate and propagate SAW up to 800°C was shown. The realization of high temperature pressure sensors based on this material is under development.

Keywords: High temperature, Surface acoustic wave, Glass-ceramic



ABS 913

EXPLORING SPARK PLASMA SINTERING AT LOW TEMPERATURE TO (CO)-SINTER FUNCTIONAL OXIDES USED IN ELECTROCERAMICS

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In a context of important development on low temperature sintering processes, we emphasize the potentiality of Spark Plasma Sintering used in specific conditions to sinter or co-sinter functional oxides. Most of the oxides used in electronic devices or energy components required high temperature to obtain high performance ceramics. The microstructure, the reactivity at interfaces (grain boundaries, multi-materials), and the defect chemistry depend on the sintering conditions (temperature, pressure, atmosphere,…) and their control critically impacts the electrical properties of ceramics. The lowering of sintering temperatures not only reduce energy costs but opens also a window towards the combination of different materials, the processing of metastable materials, materials containing metal elements with high volatility, or materials with new properties design.

We propose to highlight some strategies developed to efficiently use Spark Plasma Sintering (SPS) in the temperature range 200-900°C and to avoid the post-annealing often required to eliminate carbon contamination and chemical reduction 1. Our recent work on Micro-Electromechanical System (MEMS) energy harvesters (EH) will underline the challenge to co-sinter below 900°C and in one step complex devices such as screen-printed PbZrTiO3 in sandwich between electrodes and supported on a metallic substrate 2.The exploration of non-equilibrium sintering, through transient liquid phase, hydrated precursors, or by using solvent assisted sintering will be discussed 3-5 and illustrated in particular through our recent studies on zirconia sintered below 400°C. We will conclude by discussing complementary or synergistic effects of different low sintering temperature processes covering a very wide range of experimental conditions (from thermodynamic to strongly off-equilibrium conditions), and enabling both insightful investigation of sintering mechanisms and versatile densification capabilities for functional oxides.

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Keywords: Spark plasma Sintering, Piezoelectric Energy harvester, Zirconia

ABS 656

POROUS SILICON-TIN THIN FILMS FOR HUMIDITY SENSORS DEPOSITED BY RF MAGNETRON SPUTTERING

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Humidity is a characteristic property of atmospheres and it accounts for the amount of water vapour in air. Humidity is controlled and maintained to improve the standards of living or to improve the quality of production and of products in various industries of electrical appliances, automobile, medical and agriculture [1].
Relative humidity (RH) is one of the widely used parameter for measurement of humidity. Relative humidity is the ratio of actual vapour pressure to saturated vapour pressure at a given temperature.
Humidity sensors are based either on polymeric or ceramic materials. Humidity sensors based on ceramic materials have some advantages over polymeric material ones, such as better chemical stability and faster response to moisture. Moreover, in ceramic based sensors temperature can also be used to enhance their response time [2].
Sensitivity of humidity sensors is based on mechanisms of water adsorption on the surface and of capillary water condensation within the pores of the ceramic sensor. A porous structure allowing the increase of the surface areas, favours and enhances both the above-mentioned mechanisms: consequently an increase in the sensitivity of the sensors is expected [3].
In this work, amorphous Silicon-Tin (Si-Sn) composite thin-films with different concentrations of Sn (Tin content variation was obtained by applying 25, 50 and 75 W of power to Tin-target, while a constant power of 400 W was applied to silicon target) were produced through RF magnetron sputtering at high pressure (1.0*10-2 mbar) to obtain porous films. For each composition, two specimens were prepared and characterised. Films with lower amounts of Tin content showed amorphous structure, confirmed by XRD patterns. The porous nature of the obtained films was confirmed by the SEM, AFM and hardness measurements.
The deposited films were investigated using complex impedance spectroscopy in the frequency range of 20 Hz – 40 MHz. Si0.72Sn0.28 film was best suited for measuring changes in the relative humidity concentration. Besides the tested films, electrical response exhibited not only good repeatability but also good reproducibility.

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Keywords: Humidity sensors, Impedance spectroscopy, Composites

ABS 626

TRANSPARENT MAGNESIUM ALUMINATE SPINEL: EFFECT OF CRITICAL TEMPERATURE IN TWO-STAGE SPARK PLASMA SINTERING

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Transparent magnesium aluminate spinel is usually fabricated by pressure-assisted sintering methods such as hot pressing or spark plasma sintering (SPS) where carbon contamination occurs and impairs the optical properties. Although residual carbon can be removed by using additives, e.g. lithium fluoride, or subsequent heat treatment, its removal results in formation of light scattering centres that, in turn, impairs the transparency significantly. The present study is aimed at obtaining transparent spinel by preventing the carbon contamination using two-stage spark plasma sintering.

A commercial MgAl2O4 powder, purity > 99.0 %, was consolidated into pellets by spark-plasma sintering using graphite dies. The sintering was conducted by fast heating (100 °C min-1) of the samples, to a certain temperature between 1100 and 1200°C (hereafter referred to as a critical temperature), followed by slow heating, 2.5°C min-1, to 1250°C. A constant pressure of 80 MPa was applied at 800 °C and kept constant until the end of the SPS treatment. Afterwards, the consolidated bodies were subjected to a heat treatment at 800°C for 1h in air. Surfaces of samples were ground and mirror polished using 0.5 μm sized diamond slurries. The in-line transmission was measured on samples with a thickness of 1 mm. The distribution of carbon contamination across the width of the samples was determined using Micro-Raman Spectroscopy. Scanning electron microscopy was applied to examine the microstructure of prepared materials.

Highly dense transparent magnesium aluminate spinel polycrystalline ceramics was obtained. The samples produced at the critical temperature of 1150°C showed the maximum transparency, Tin=75% at λ=550 nm. Raman spectroscopy analyses showed that the samples were contaminated by glassy carbon. The contamination increased with the increase of the critical temperature, and it was concentrated at the centre of the sample. This indicates that carbon contamination occured through precipitation of carbon-containing gases into the samples during densification. Thermodynamic calculations revealed that the trapped glassy carbon was a product of reactions between carbon and spinel, and resulted from the local temperature increase during the intermediate stage of sintering. Carbon contamination can be thus avoided by reducing the heating rate before the final stage of densification. Two-stage SPS paves the way for preparation of highly transparent polycrystalline spinel ceramics without the use of sintering additives.

Keywords: MgAl2O4,SPS,two stage sintering

ABS 911

EFFECT OF THE RGO (REDUCED GRAPHENE OXIDE) ADDITION ON CONDUCTIVITY AND MICROSTRUCTURE OF CERAMICS ZrO2-Y2O3 SINTERED USING DIFFERENT TECHNIQUES

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Nowadays, the development of the novel nanoceramic materials with unique characteristics is one of the major directions in the material science. The use of nanosized precursors for such materials manufacturing makes it possible to design their chemical, physical and mechanical properties. Powder particle properties (i.e. particle size distribution, mean size, agglomeration degree etc) strongly affect on the final microstructure and properties of the ceramics. Here the control of grain growth during ceramics sintering is regarded critical to achieve nanoceramics. In some studies it has been shown that graphene (Gr) and reduced graphene oxide (rGO) addition can act as effective grain growth retarding agent in metal-matrix composites, aluminum, nickel and copper, in particular. However, the state of carbon additive, and, consequently, the properties of the resulting ceramic material strongly depend on the method of compaction and sintering. Thus the aim of the present work was the manufacturing of rGO-zirconia based nanocomposites by three different techniques: in air, in vacuum (10-5) and in closed volume without oxygen access at the same temperature of 1550°C with the following the investigation of the effect of rGO addition on microstructure, phase composition and conductivity. 9Y2O3-91ZrO2 (mol.%) was chosen for the investigation (Yttria Stabilized Zirconia - YSZ). Reduced graphene oxide was synthesized via Hammers method with following microwave exfoliation. Based on rGO characteristics and particle size distribution the amount of rGO addition was calculated. Precursor powder YSZ was synthesized by the sol-gel synthesis in a variation of reverse co-precipitation of inorganic saults. Via SEM, EDX, XRD, STA and Raman spectroscopy and impedance spectroscopy it was shown that carbon additive burns out during synthesis on air, thus the microstructure and ratio of volume and surface conductivity changes. After sintering in vacuum and in in closed volume the carbon phase and microstructure changes was found but without significant change in conductivity. The research was performed with the support of Research Park of SPSU.

Keywords: yttria stabilizied zirconia, reduced graphene oxide, conductivity

ABS 908

IMPROVING STATE-OF-THE-ART STRONTIUM FERRITE MAGNETS: STRATEGIES TO OPTIMIZE MAGNETIC AND MICROSTRUCTURAL PROPERTIES

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Permanent magnets are ubiquitous materials in both industry and society, for their ability to create spontaneous magnetic fields, such as in energy generation, transformation and storage, biomedical applications (RMN, sensors), information storage, and for daily household applications. Ferrites and Rare-Earth (RE) based permanent magnets (Sm or Nd) have been dominating the market for decades, but RE-magnets, due to their better magnetic performances, are employed in highest impact technologies. However the REs are considered critical raw materials as China controls almost 97% of RE- mining and RE-magnets production and export quotas. As a consequence, research has emerged whose main goal is to find alternative magnets that can substitute RE ones in selected applications. One of the most promising routes to obtain alternatives to RE magnets is to fabricate metal/oxide composite magnets based on a hard magnetic phase with high coercivity and a soft magnetic phase with high magnetization [1,2]. The optimization the microstructural properties of the individual phases is a critical condition in order to ensure an improvement of the magnetic properties, in particular the remanence, in these new permanent magnet.

This work will focus on the optimization of microstructural and magnetic properties of the components of the composites formed by magnetically hard Strontium hexaferrite and soft metallic FeCo nanowires, through synthesis and processing. On one hand, thermal treatments are employed to control the particle size and crystal structure of the hexaferrite grains. On the other hand, the method to tailor the diameters of nanowires will be illustrated. We have observed that the coercivity of the hexaferrite drastically decreases with the increasing of the grain size above 1100°C. Various solutions to solve this issue are presented and discussed, emphasizing the use of additives that act as grain inhibitors.

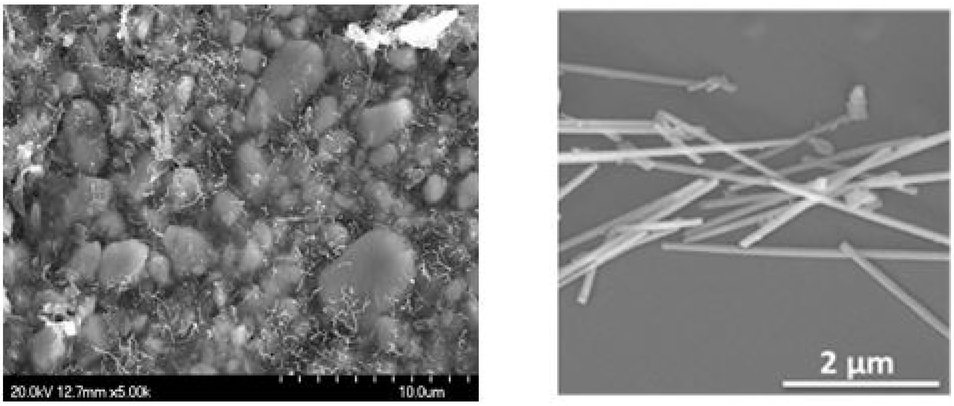

Figure 1.SEM micrograph of magnets for injection molding and SEM micrograph of nanowires (D=30nm).

1L. H. Lewis and F. Jiménez-Villacorta, Metallurgical and Materials Transactions A 44, S2 (2013).
2A. Quesada, C. Granados-Miralles, A. López-Ortega, et al. Adv. Electron. Mater. (2016) 1500365.

We acknowledge funding from the European Commission through the project AMPHIBIAN (H2020-MNBP-2016-720853).

Keywords: Hard and soft magnetic ceramic

ABS 573

LAYERED CERAMIC COMPOSITE SYSTEM FOR APPLICATION AS TEMPERATURE SENSOR

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At the dawn of industry 4.0, highly specialized sensors gain ever growing significance. High temperature processes in confined or moving systems, such as the combustion in jet engines or blast furnaces, require a precise and wireless measurement method.
Closely above their Curie point, ferroelectric ceramics exhibit a very defined permittivity over temperature relation. This can be utilized to create temperature-sensitive microwave resonators, which can be read out wirelessly. These devices are mainly limited via their dielectric loss, which, if too high, impedes the recognition of the backscattered signal amongst the clutter. Layered ceramic composite structures consisting of a temperature sensitive and a low loss material promise the best properties for this kind of application.

The layered ceramic composites were prepared from Ba0,6Sr0,4TiO3 (BST), which provides excellent temperature sensitivity, and Mg3B2O6 (MBO), which shows very low dielectric loss at microwave frequencies. Both materials were granulated, pressed into pellets and sintered. This was done separately, to avoid interface reactions, which were observed when both materials were pressed and sintered as layered green . The dense pellets were combined into a layered structure by interconnection with MBO screen printing paste and dried. were sintered at a lower temperature compared to the separate pellets, to form a mechanically stable layered structure with defined interfaces. The dielectric properties were determined by means of impedance spectroscopy and wireless measurements.

Sintering of a layered green led to heavy detrimental interface processes, rendering the creation of a layered sample via this path very difficult. Mechanically stable layered ceramic composites with defined interfaces were obtained by separate sintering and layering with screen printing paste. Small amounts of Titan could still be observed in the dielectric layer. The expected dielectric behavior was confirmed via wireless measurements.

The successful fabrication process for layered ceramic composites is not dependent on the individual sintering properties of the participating materials. It can therefore be used to better modify dielectric behavior of different ceramics as long as the inclination of the incoming electromagnetic signal is known. Apart from sensors, low losses are an important factor in most microwave applications, so layered structures have the potential to reduce energy consumption and heat buildup in a variety of devices.

This project was made possible by the financial support of the DFG (GZ:BI 1636/6-1 & JA 921/63-1).

Keywords: Ceramic Composite Materials, Sensor application, Special composite layout

ABS 570

TOWARDS TAILORED POROSIFICATION OF LTCC SUBSTRATES: STUDY OF THE ETCHING PROCESS

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Low temperature co-fired ceramics (LTCC) technology has been successfully used in microelectronics and as a compact packaging solution for automotive and telecommunication applications. However, their generally high permittivity is unfavourable for micromachined devices operated at high frequencies. Due to this drawback, we have established a wet-chemical etching process as an effective approach which can be applied to LTCC substrates in their as-fired state and allows their local permittivity reduction in the regions of interest. However, the main challenges associated with this method are controlling the degree of porosification while preserving the surface quality. Therefore, in the present work, we report on applying phosphoric acid at temperatures below 100°C as a very efficient approach to achieve a tailored porosification of LTCC substrates. Phosphoric acid solution from Sigma-Aldrich was used for the etching of commercially available L8 LTCC substrates from Ferro Corporation (Ferro L8). All etching experiments were conducted at a constant temperature in a capped beaker with a polytetrafluoroethylene (PTFE) fixture for holding the substrates in position. After etching, samples were thoroughly washed with deionized water and isopropanol and were characterized by different techniques including SEM, TEM, EDX, XRD, and porosimetry. Moreover, the etching mechanism was further investigated through gravimetric and penetration depth investigations.
The micrographs of as-fired and etched LTCC substrates (Fig. 1) illustrate the great performance of the method for porosification of LTCC where very deep etching in a relatively short etching time (2 hours) with a high-quality surface is realized. The improved surface quality features a suitable bearing plane for further metallization lines. Furthermore, investigating the impact of essential etching parameters including etch time, bath temperature, and etchant concentration shows that due to the decreased viscosity, higher temperatures and reduced etchant concentrations are more favorable for the etching process. However, too high temperature results in an extremely destroyed and roughened surface and a too diluted etchant cannot provide sufficient adducts for the dissolution reaction and therefore the rate of dissolution will be decreased. Further discussion on the obtained results will be presented in the final conference paper.

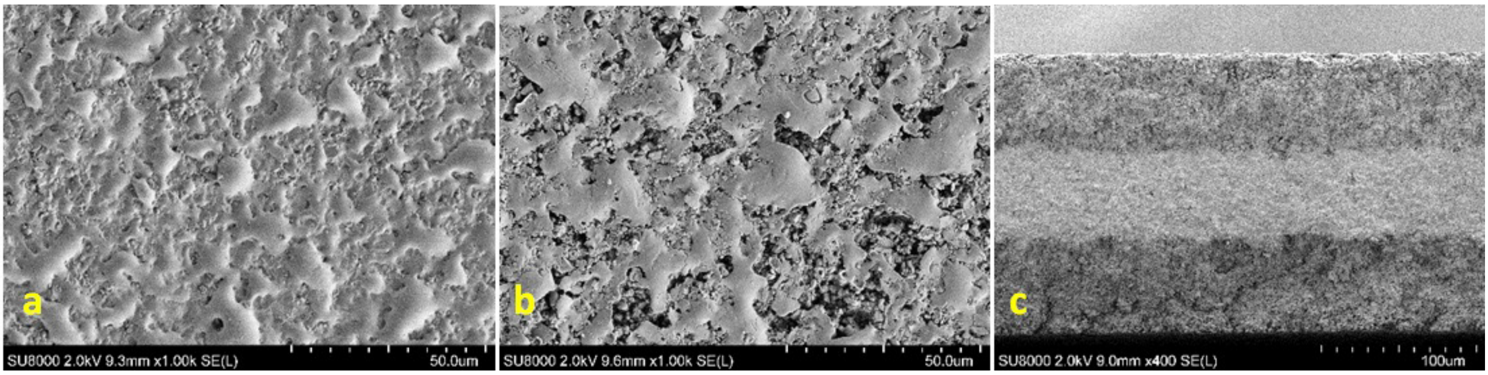

Fig.1: SEM images of LTCC samples a) as-fired, b) etched (top-view), and c) etched (cross-section).

Phosphoric acid at temperatures below 100°C is an appropriate etchant for porosification and thereby permittivity reduction of Ferro L8 LTCC substrates. By controlling the etching parameters including bath temperature, etchant concentration and etch time, a tailored porosification with a high-quality surface is realized.

Keywords: LTCC, Permittivity reduction, wet-chemical etching

ABS 924

FABRICATION OF THIN TRANSPARENT CERAMICS FROM THIN GREEN BODIES

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Transparent ceramics are a group inside functional ceramics, which combine the typical properties of ceramics, such as high hardness, strength and chemical resistivity with optical functionality. Several applications, like use for ballistic protection, require relative thick parts of a typical thickness in the range 2-8 mm. For applications, such as protection windows of displays of electronic devices for service with higher mechanical load, as for touchscreens of smartphones or tablets thinner parts are required. The fabrication of thin, large area parts with near net-shape thicknesses, size accuracy and planarity is so far associated with a time- and cost-consuming finishing treatment after sintering.

For fabrication of transparent ceramics highly pure (and thus, expensive) starting powders have to be used a as well as a cost-intensive technological chain in order to reach the required low porosity. Thus, decreasing the thickness of the part by decreasing the thickness of the green bodies is an important contribution for reduction of the production costs.

In this contribution, recent efforts to produce thin transparent spinel, zirconia and alumina ceramics from thin green bodies using dry pressing /CIP or gelcasting as shaping technologies are summarized. After reaching thin green bodies with small lateral dimensions efforts were made in order to increase these dimensions.

As one example, planar green bodies made of spinel with a maximum length of 160 mm in one direction and thicknesses below 1 mm using uniaxial and cold-isostatic pressing were prepared. After a multi-step sintering procedure, highly dense transparent parts with a maximum length of 110 mm in one direction, and a thickness in the range 0.5 – 0.8 mm were obtained. After applying a double-sided grinding, lapping and polishing process these transparent plates showed a high optical transparency near the theoretical limit and a low haze < 2 %.

Keywords: thin transparent ceramics, spinel, alumina

ABS 905

SODIUM BISMUTH TITANATE-BASED HIGH TEMPERATURE CAPACITOR MATERIALS

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There is an increasing demand of electronic components for sensing and controlling purposes in harsh environments. Hence, the properties of these electronic circuitry need to be stable over a large temperature range, with maximum temperatures well beyond 200°C. Apart from ceramics, there is no competitive capacitor material which can endure these temperatures. Nevertheless, many ceramic materials used for capacitor applications undergo phase transitions at these elevated temperatures, which result in an increase of permittivity and dielectric loss. Therefore, it is difficult to obtain a stable temperature-independent capacitance.

Recently, promising lead-free solid solutions of sodium bismuth titanate (NBT) have been presented which have unique properties, rendering them as excellent materials for possible capacitor applications. However, a major problem remains the high dielectric loss. In order to reduce this dielectric loss, the defect chemistry for such a critical high-temperature component has to be well understood.

In this study, the influence of A-site non-stoichiometry in NBT-based materials is investigated, especially regarding its impact on the properties for high-temperature capacitor applications. For this, the temperature-dependent permittivity, dielectric loss and polarization are measured. The studied materials show a significantly broad temperature regime from -70°C up to 360°C with large temperature-independent permittivity, as well as low loss factors. It has even been possible to show that all investigated materials can compete with the energy density of a commercial X7R. Furthermore, an excellent energy efficiency of 97% can be reached.

Keywords: high-temperature capacitor, sodium bismuth titanate, defect chemistry

ABS 904

FABRICATION AND LUMINESCENCE OF CE-DOPED GALLIUM GADOLINIUM ALUMINUM GARNET TRANSPARENT CERAMICS MADE BY TWO-STEP REACTION SINTERING

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Ce-doped garnets find their use as scintillators as well as phosphors. Among synthetic garnets, gallium gadolinium aluminum garnet (GGAG) is a relatively new and interesting material, a mixed garnet that has displayed very good scintillation and luminescent properties [1].
In the presented work GGAG ceramic samples were produced by reaction sintering from commercial oxide powders. The mixed powders were pressed into pellets and sintered. In order to achieve transparency of a ceramic material, it is crucial to eliminate porosity. Therefore, the sintering process was carefully selected and the use of sintering additives was studied. The sintering process consisted of two steps, viz. sintering in air followed by hot isostatic pressing. The influence of starting powders, sintering additives and sintering conditions on the microstructure and optical quality of the ceramics was studied. Fig. 1 shows one of the ceramic samples and its microstructure.

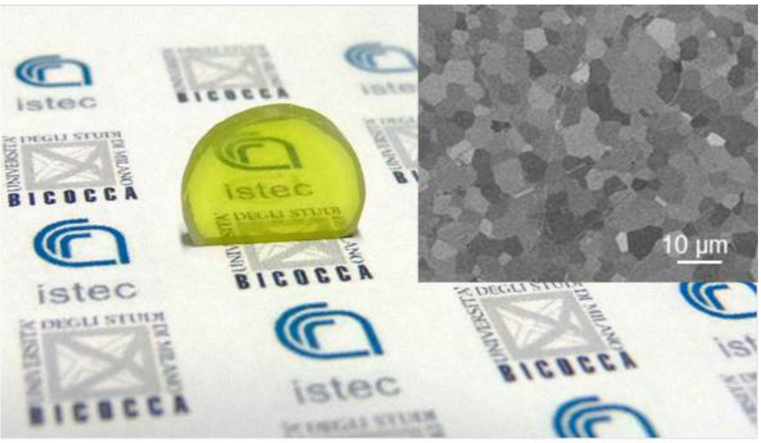

Figure 1. Photograph and a SEM micrograph showing a Ce:GGAG transparent ceramic sample and its microstructure.

Luminescence properties were studied by means of photo- and radio-luminescence and correlated to the fabrication process parameters. In some of the samples, significant persistent luminescence was observed and studied. Moreover, point defects were investigated by thermally stimulated luminescence, also in comparison with a single crystal with the same composition.

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Keywords: Gadolinium Gallium Garnet, Transparent ceramics, Luminescence

ABS 902

GRAIN SIZE-DEPENDENCE OF FUNCTIONAL PROPERTIES IN SOME $BaTiO_3$-BASED CERAMICS

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A and B-site homovalently-substituted BaTiO3 nanopowders were prepared by wet chemical routes, as sol-gel and Pechini method. Electron microscopy investigations emphasized the significant influence of the synthesis conditions in controlling particle size and morphology.
BaTi1-xZrxO3 (BTZ) (x = 0 - 0.20) ceramics were elaborated by alternative sintering procedures from nanopowders synthesized by the modified Pechini method. The dielectric and ferroelectric properties in micro- and nano-structured BTZ ceramics consolidated by conventional sintering and spark plasma sintering (SPS) were comparatively analyzed. It was found that, for undoped BaTiO3, as well for the BTZ ceramics with lower Zr content (x <= 0.15), the decrease of grain size determines the shift of the Curie temperature toward lower temperature values, as well as a strong reduction of both the ferroelectric switching and permittivity maxima, which become diffuse, proving a ferroelectric-relaxor crossover. For the highly-substituted BTZ ceramics (x = 0.20), reducing grain size to the nanometric range involves the gradual vanishing of ferroelectric-paraelectric phase transition and the evolution towards temperature-independent permittivity values, as in the case of low-permittivity dielectrics. The influence of grain size on the dielectric and pyroelectric behaviour was also investigated for Ba1-xSrxTiO3 (BST) (x = 0 - 0.30) ceramics derived from powders synthesized by the acetate variant of the sol-gel method and consolidated by conventional sintering and spark plasma sintering, respectively. It was found that by reducing grain size from micro-scale toward nano-scale, the permittivity values decreased by approximately one order of magnitude over the whole investigated temperature range. However, for the nanostructured BST ceramics, no significant shifts of the Curie temperature values, with respect to those specific to the microstructured ceramics, were recorded. Sharp permittivity maxima were obtained, proving that the first-order phase transitions were maintained. In order to improve the pyroelectric properties compositionally graded samples were prepared by an innovative procedure. The variation of the solute content across the thickness of the ceramic samples also induced a grain size gradient, which contributes to a strong flattening of the temperature dependence of the dielectric constant and to the increase of both pyroelectric coefficient and figure of merit.

Keywords: BaTiO3,ferroelectric-paraelectric,pyroelectric behavior

ABS 901

SPECTROSCOPIC AND TERAHERTZ RESPONSE OF Er^{3+}/Yb^{3+} DOPED $La_2Zr_2O_7$ CERAMICS

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Lanthanum zirconate ceramics with the pyrochlore structure co-doped with Er3+/Yb3+ are efficient mediators for nir-IR radiation up-conversion. Utilisation of such materials can offer distinct functionality in sensors, efficiency enhancement of UV-VIS devices and/or detectors for specific military applications. Characteristic absorption coefficient and refractive index frequency dependence of Er3+/Yb3+ co-doped La2Zr2O7 ceramics by the Terahertz time-domain spectroscopy was done for the first time. Such measurements can be helpful for better understanding of electron energy transfer by mechanisms considered, e.g. as Förster resonant nonradiative energy transfer (FR-NET) or phonon-assisted nonradiative energy transfer (PA-NET). Clearly detected low frequency band resulting from Er3+ doping element was found at about 0.9 THz. At the same time the observation of gradual peak intensity increase according to Er3+ growing concentration used for the doping was found.

Acknowledgement The financial support of the Slovak Grant Agency for Science VEGA grant No. 1/0278/16, 1/0906/17 and 1/0527/18 and Slovak Research and Development Agency APVV-16-0341 are greatly appreciated. This work is also based on the results of the project Center for Applied Research of New Materials and Technology Transfer, ITMS 26240220088, supported by the Science and Research Operational Program by the European Regional Development Fund.

Keywords: Terahertz-time domain spectroscopy, Far-infrared, Dielectric properties, Rare earths doping, Lanthanum-zirconates

ABS 900

COMBINATION OF STRUCTURAL AND MICROSTRUCTURAL EFFECTS IN THE MULTIFERROIC RESPONSE OF Nd AND Ti CO-DOPED BiFeO$_3$ BULK CERAMICS

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BiFeO₃ (BFO) is well-known to be a promising multiferroic material due to its high phase-transition temperatures, which could make it able to exhibit room temperature ferroelectricity and ferromagnetism. Both properties directly derive from a perovskite-like structure that at atmospheric pressure and room temperature presents a rhombohedrically distorted perovskite structure belonging to the R3c group. However, BFO materials present several drawbacks mainly related to three different aspects. The first one would be the difficulty in obtaining this material free of secondary phases [1]. The second one is related to a weak electric response, and this includes a low remnant polarization, a high coercive field, a low dielectric constant, low piezoelectric coefficients and, probably the most relevant from the electrical point of view, a high leakage current [2]. Finally, the third drawback is linked to the existence of a spiral spin modulation which cancels any spontaneous net magnetization in the consolidated material [3]. In order to overcome this adverse scenario different strategies have been attempted, and among them, chemical modification of BiFeO₃ is recognized as a potentially useful approach [4]. Neodymium substitution onto the A site of the perovskite lattice provokes significant changes in the crystal structure of the parent material which can derive in enhanced multiferroic properties, but the conductivity in the bulk system is still too high. Titanium doping, on the other hand, generates a distinctive micro-nanostructure in the consolidated ceramics which can largely increase the dc resistivity of the whole material. In this work, the concurrent doping of BiFeO₃ with neodymium and titanium returns a remarkable improvement of the multiferroic possibilities of the bulk ceramics. No explicit chemical interactions between both dopants are ever found and so the co-doped material capitalizes on the structural and microstructural benefits provided by each element. The resulting co-doped material displays a reduction of the leakage currents, an effective macroscopic piezoresponse and an improved ferromagnetic behaviour which is not easy to attain in BiFeO₃ bulk ceramics.

Acknowledgments: This work has been conducted in the frame of MAT2016-80182-R and MAT2014-59210-JIN research projects.

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Keywords: Multiferroics, BiFeO₃,Doping

ABS 899

ANISOTROPIC FERRITE-BASED HYBRID MAGNETS CONSOLIDATED BY SPARK PLASMA SINTERING: TOWARDS RARE-EARTH-FREE MAGNETS FOR ENERGY STORAGE

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The intensive research of ferrite-based ceramic permanent magnets has again been revived, due to the so-called rare-earth crisis. [1, 2] In particular, a quest to enhance ferrites' energy product (BHmax), is still underway. Large BHmax values are found in magnets combining substantial magnetisation at remanence (MR) with high coercivity. Both parameters are influenced by materials properties, such as crystalline and shape anisotropy and particle' size. Here, the influence of composition, particle size, sintering conditions and exposure to the external magnetic field before compaction on microstructure and consequently magnetic properties of strontium ferrite (SFO)-based hybrid composites will be presented. Powders' mixtures of commercial SFO powder consisting of micron-sized, isotropic particles, or alternatively hydrothermally (HT) synthesised SFO with hexagonally-shaped platelets with a diameter of 1 micron and thickness up to 100 nm, and a soft magnetic phase, (Mn,Zn)-ferrite with high magnetization, in various ratios were sintered with Spark Plasma Sintering (SPS) furnace. Starting powders and hybrid magnets were examined by means of phase composition (XRD) and microstructure (TEM, SEM). Their magnetic properties were evaluated with vibrating sample magnetometer and permeameter. Depending on the concentration and composition of the soft phase the MR of the composite can be altered. Application of external magnetic field before the consolidation induces the anisotropy in commercial, and HT synthesised SFO, leading to the increase in the MR of hybrid magnets. Moreover, sintering with SPS promotes the alignment of HT synthesised SFO particles in the axial direction of the applied pressure, which is also the direction of SFOs' easy axis and thus the enhancement in MR is perceived leading to the MR/MS higher than 0.7. Besides, after SPS almost no grain growth was observed, which is beneficial for exploiting advantages of nanosized-induced phenomena also in bulk sintered samples.

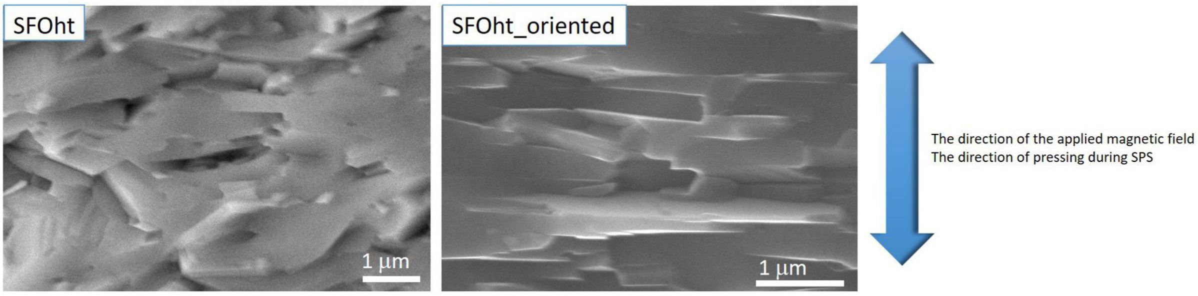

Figure 1: Hydrothermally synthesized strontium ferrite after SPS sintering. Left: randomly oriented particles, and right SFO particles aligned with the direction of the applied magnetic field.

Acknowledgement: for financial support from the European Commission through the project AMPHIBIAN (H2020-NMBP-2016-720853).

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Keywords: Anisotropic ferrites, Spark Plasma Sintering, Magnets for energy storage

ABS 897

MICROSCALE ELECTRICAL CHARACTERIZATION AND MODELLING OF THE HIGHLY NON-LINEAR ELECTRICAL BEHAVIOR OF ZnO VARISTOR CERAMICS

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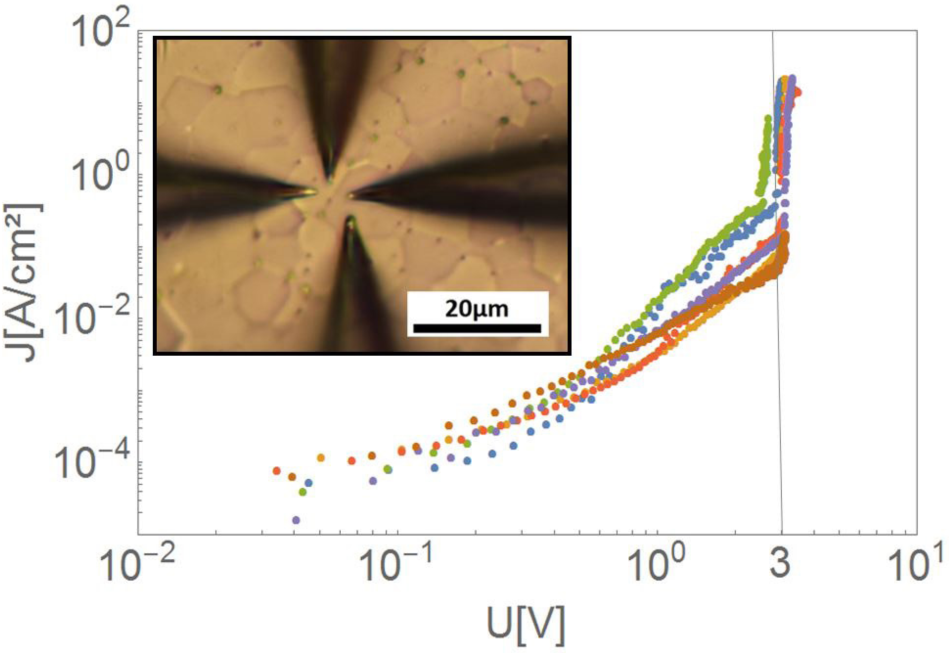
ZnO varistors are the leading overvoltage protection elements in today's electronic industry. Their highly non-linear current-voltage characteristics, very fast response times, good reliability and attractive cost of production are unique in this field. Yet, there are challenges and questions to be addressed. Especially, the urge to create even smaller, more versatile and reliable parts that fit industry's demands brings manufacturers to the limits of their capabilities. Since the electrical behavior of ZnO varistors is strongly affected by the microstructure of the sintered material, especially the grain boundaries, a comprehensive investigation, considering both the effects at the grain boundaries and the influence of the complex microstructure, is needed for supplying knowledge necessary for device improvement.

In this work complementary experimental methods and computer supported modelling is used as a basis for describing and predicting varistor behavior. The first experimental method being presented here is the micro lock-in infrared thermography to detect very subtle heat differences in the microscale range and to identify preferential current paths through the ZnO ceramic. A complementary technique is the micro 4-point probe method where the tips of two very fine needles are placed at two different ZnO grains at a time. (See inset image below.) With this method the current-voltage characteristics of single grain boundaries can be measured. (See figure below.) The grains and the grain boundaries form a three-dimensional network (i.e. the micro structure) of resistors. This resistor network is solved numerically, reproducing current-voltage characteristics of real components. It was found that the electrical behavior of low-voltage varistors can be determined by a few or even a single grain boundary.



Current-voltage characteristics of a grain-to-grain contacts in a varistor

Keywords: varistor, ZnO, Schottky contact

ABS 512

TRANSPORT PROPERTIES OF $LaNiO_3$-La_2CuO_4 HETEROSTRUCTURES

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Transition-metal oxides present a wide range of electronic properties ranging from insulating to semiconducting and even superconducting behavior [1]. It is well-known that the electrical transport along interfaces [2] can be improved or suppressed by several orders of magnitudes, and various examples such as $LaAlO_3$/$SrTiO_3$ interfaces [3], La_2CuO_4/$La_{2-x}M_xNiO_4$ (M: Ba^{2+}, Sr^{2+}, and Ca^{2+}) interfaces [4, 5], and $SrTiO_3$ [6] were extensively studied. Moreover oxygen stoichiometry and exchange dynamics are also important at these interfaces [7, 8]. Hence, the utilization of interface engineering and linking it with defect chemistry can be a powerful tool to tailor the electrical transport properties of oxides.

In this study, by means of the atomic-layer-by-layer oxide molecular beam epitaxy technique (ALL-oxide MBE), we designed oxide heterostructures consisting of tetragonal K_2NiF_4-type insulating La_2CuO_4 (LCO) and perovskite-type metallic $LaNiO_3$ (LNO) layers with different thicknesses to assess the heterostructure–thermoelectric property–relationship at high temperatures. The temperature dependence of the Seebeck coefficient S(T) and the electrical conductivity σ(T) were measured simultaneously under 1 bar oxygen between 300 K-800 K, using ULVAC ZEM3 system for S(T) and σ(T) measurements

We have observed that the transport properties depend on the constituent layer thickness, interface intermixing, and oxygen exchange dynamics in LCO layers, which occurs at high temperatures. As the thickness of the individual layers was reduced, the electrical conductivity decreased and the sign of the S(T) changed, revealing the contribution of the individual layers where the possible interfacial contributions cannot be ruled out. High-resolution scanning transmission electron microscopy (HR-STEM) investigations showed that a substitutional solid solution of $La_2(CuNi)O_4$ was formed when the thickness of the constituent layers was decreased. Moreover, in LNO-LCO heterostructures with relatively thick LNO and LCO layers (8 u.c. and 6 u.c. thick) we have demonstrated that the thermoelectric properties are determined by the more conducting LNO layers and can be described by the parallel slab model.

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Keywords: Epitaxial growth, Oxide interfaces, Thermoelectricity

ABS 896

EFFECT OF BORON ON MICROSTRUCTURAL EVOLUTION DURING CRYSTALLIZATION OF LONG AFTERGLOW STRONTIUM ALUMINATE COMPOUNDS

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Strontium aluminate ceramics, when co-doped with Eu2+ and Dy3+, have an impressive capability for temporary storage and slow release of light, making them attractive for zero-energy consumption lighting. In such materials, the addition of B2O3 as a sintering flux not only facilitates the sintering process through modifying the crystallization kinetics, but also increases the brightness and dramatically extends the afterglow persistence of strontium aluminate powders [1,2].

To understand the mechanisms by which B extends the afterglow, we have analyzed the microstructure under thermal and kinetic control by a series of experiments. In this talk, we first present a detailed thermal analysis study to determine the effect of B2O3 on the microstructural evolution of stoichiometric Sr4Al14O25 during Pechini processing, i.e., from the amorphous gel formed by polymerization of ethylene glycol and citric acid-chelated cations. Our results reveal that SrCO3 forms as a by-product during sol-gel processing of the amorphous precursor, and it decomposes at around 900°C in the absence of B2O3. Metastable SrAl2O4 starts to form from the amorphous precursor at the 1st exotherm with an onset at 930 °C, which corresponds to transformation of theta-Al2O3 to alpha-Al2O3. Beyond the 1st exotherm, the amount of SrAl2O7 phase increases, while SrAl2O4 starts to disappear. The target phase Sr4Al14O25 evolves from SrAl4O7 over a wide temperature range starting from the onset of second exotherm at 1110°C and continuously forms with increasing temperature, indicative of a diffusion-limited mechanism for formation of Sr4Al14O25. The presence of B2O3 accelerates the formation of Sr4Al14O25 by facilitating decomposition of SrCO3 at lower temperatures, thereby providing more available Sr to react with the nearby SrAl4O7 to form Sr4Al14O25.

Because subtle changes in number and in spatial arrangements of atoms in the first nearest neighbor shell around an ionized atom result in characteristic differences in the shape of energy loss near edge fine structure (ELNES) features, we acquired EELS spectrum images to evaluate the nature of boron incorporation into the microstructure of a conventionally sintered specimen prepared from amorphous precursor of Sr4Al14O25: 1 mol% Eu, 1 mol% Dy, 30 mol% B2O3 (S4A7EDB) compound. By mapping the B-K ELNES, our results indicate that boron coordination is 4-fold ([4]B) in a SrAl4O7 crystal, and 3-fold ([3]B) in the amorphous intergranular pockets.

Keywords: Long Afterglow, Thermal Analysis, B-K ELNES

ABS 500

MICROSTRUCTURAL EVOLUTION AND RELEVANT MECHANICAL PROPERTIES OF TRANSPARENT Al-RICH MAGNESIUM ALUMINATES

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Objective In this study, we report the fabrication of Al-rich spinel with suppressed grain growth with increasing Al₂O₃ content and thus without deterioration of mechanical properties. The mechanism of grain growth suppression will be suggested by analyzing the detailed microstructure by SEM.
Materials & Methods On the basis of MgO-nAl₂O₃, transparent ceramics having three compositions of n = 1.2, 1.5 and 2.0 were prepared. MgAl₂O₄ and Al₂O₃ were mixed in DI water and ball-milled for 24 h. After the microfluidization was applied to remove the agglomerates of the raw powder, the slurry was freeze-granulated using an ultrasonic atomizer. The dried granules were shaped and cold isostatic pressed under 200 MPa for making green bodies. After burn-out of dispersant, the green bodies were sintered at 1200~1600^oC for 2h to analyze the sintering behavior and remove open pores prior to the hot-isostatic press at 1750^oC.
Results Figure 1 shows in-line transmission and photographs. Fig. 1(b) is a photograph taken at 50 cm away from the background. As the value of n increases, the text becomes clearer, indicating that the transmittance increases. Fig 1.(c) is a photograph focused on specimens with a black paper background; the number of scattering sources with a size of several tens μm in the specimen gradually decreases with increasing value of n. It is considered that it affects the apparent permeability. The in-line transmittance in Fig. 1(a) is consistent with photographs; spinel with incresed n value showed the higher transmittance.
Figure 2 shows the strength and the microstructures. The microstructure of the sintered was remarkably different by composition change. For n = 1.2, the median grain size was about 15 μm with bimodal grain-size distribution. For n = 1.5, the grain size was about 10 μm and bimodal distribution was also shown. On the other hand, in case of n = 2.0, the grain size was about 5 μm and the size distribution was uni-modal. It is considered that the strength of n = 2.0 specimen is highest due to the suppression of grain growth.
Conclusions We have succeeded in fabricating transparent Al-rich spinel ceramics with suppressed grain growth. The inhibition of grain growth was determined by the presence or absence of Al₂O₃ before the HIP treatment, and the grain growth mechanism with different compositions was suggested based on the microstructural analysis.

Keywords: Magnesium Aluminate, Microstructural evolution, Mechanical properties

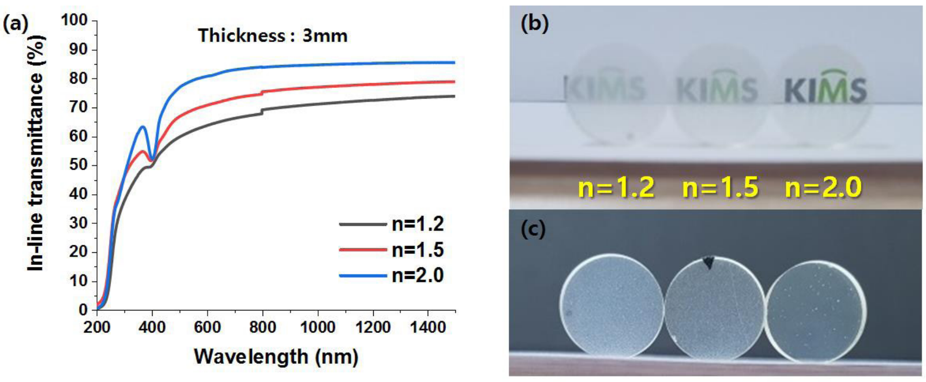

Fig 1. (a) In-line transmittance of Al-rich magnesium aluminates and (b), (c) photographs

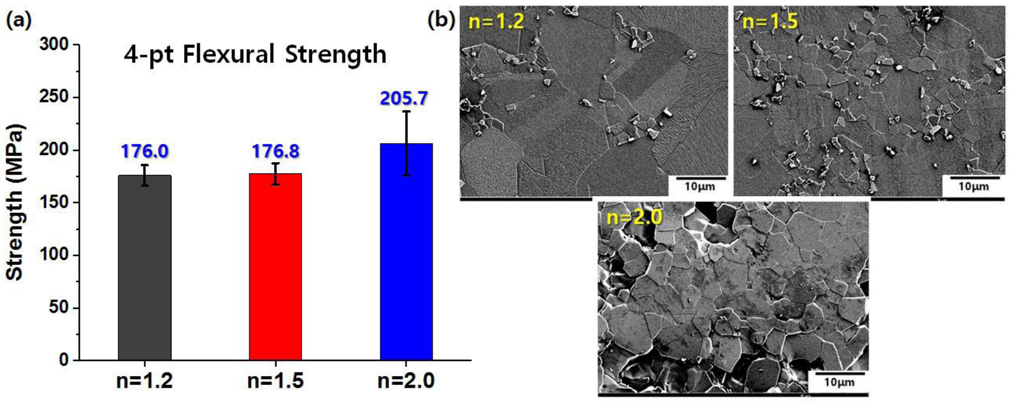

Fig 2. (a) Flexural strength and (b) microstructures of Al-rich spinel ceramics

ABS 498

GIANT STRAIN OF LEAD-FREE BISMUTH FERRITE–BASED PIEZOCERAMICS

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Objectives Environmental apprehensions are intensely driving the need to replace the lead (Pb)-based ceramics. The current article describes both processing and compositional approaches to achieve enhanced piezoelectric properties in Pb-free BiFeO3-based materials.

Materials and Methods Lead-free solid ceramics series of (BiNa0.84K0.16)0.48Sr0.04TiO3-modified 0.65Bi1.05FeO3–0.35BaTiO3 (BFBT–xBNKS, where x = 0–0.10) ceramics were synthesized by solid-state reaction technique, followed by air quenching process. The same fabrication route and electrical characterizations were performed according to our previously published article [1].

Results The room temperature (RT) X-ray diffraction (XRD) patterns show a stable solid solution and pure perovskite (ABO3) phase within the detection limit of XRD. All samples have fairly compact and dense microstructures with increasing trend in the average grain size and relative density (> 95%) by the addition of BNKS content in BFBT ceramics. A pronounced variation in dielectric properties with temperature was observed in all selected composition range of BFBT–BNKS materials. At 4 mol% BNKS addition in BFBT piezoceramics, significantly large strain (870 pm/V) at low driving field 4 kV/mm with high maximum temperature (Tmax) was observed.

Conclusion Lead-free (BiNa0.84K0.16)0.48Sr0.04TiO3-modified 0.65Bi1.05FeO3–0.35BaTiO3 (BFBT–BNKS) piezoceramics have been fabricated by a solid state reaction method, followed by air quenching and their crystal structure, microstructure and electrical properties were explored experimentally. The XRD patterns proved that all the BNKS-modified BFBT ceramics showed no remarkable change in the crystal structure. Variation in the average grain size, relative density, enhancement in the maximum temperature (Tmax), polarization (Pmax and Prem) and field induced strain response were observed by the addition of BNKS in BFBT system. At the room temperature, for the BNKS = 0.04 composition, a giant piezoelectric coefficient (d*33) of 870 pm/V at 4 kV/mm was experiential. This improvement in electromechanical strain and the high Tmax can be attributed to the (BiNa0.84K0.16)0.48Sr0.04TiO3 modification and quenching mechanism as well, which make the system useful for high-temperature actuator applications.

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Keywords: Lead-Free, Ferroelectrics, Field-induced Strain

ABS 894

DISLOCATION NETWORK AS MECHANISM FOR RETAINING BISMUTH AT (0001) INVERSION BOUNDARIES IN PIEZOTRONIC ZnO BICRYSTALS

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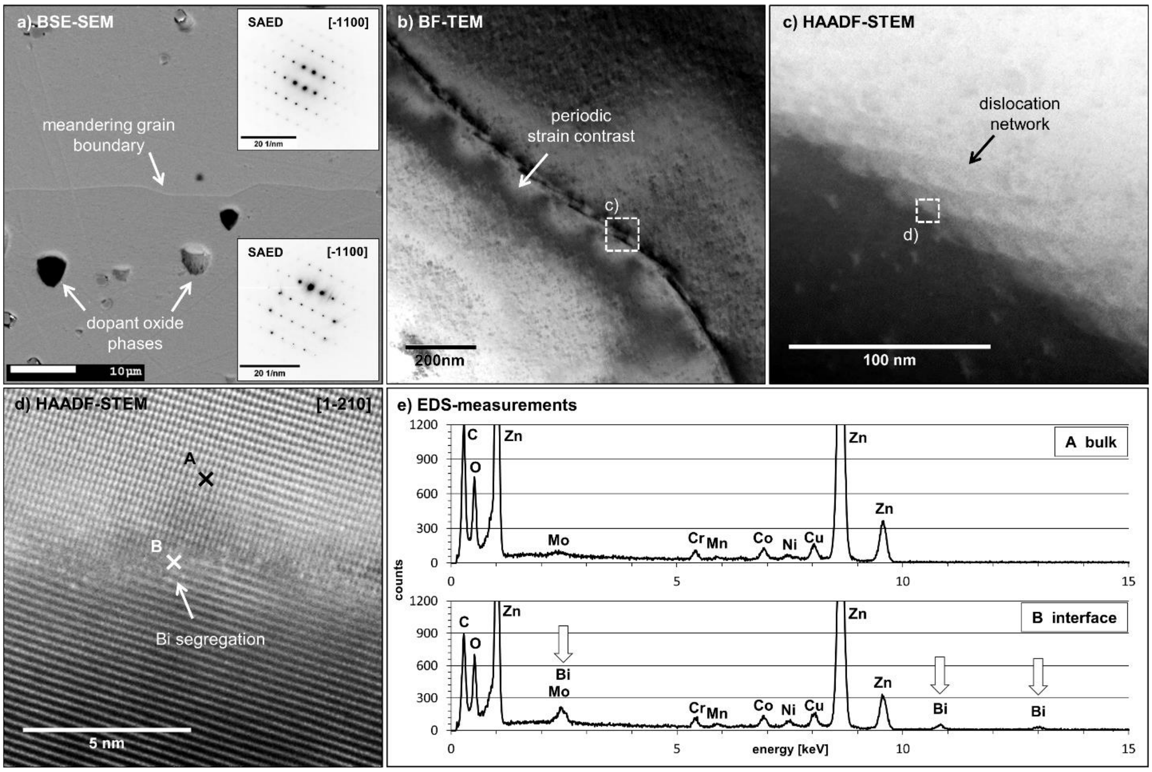
TEM and SEM investigations of ZnO bicrystal interfaces synthesized by epitaxial solid-state transformation revealed a distinctive relationship between the formation of grain boundary dislocations and the stable incorporation of large dopants ion, such as bismuth. This synthesis method generates a strained meandering grain boundary with a localized network of dislocations, which facilitates the dopant incorporation essential for the creation of varistor type potential barriers. This bismuth retaining mechanism is of special interest for the design of piezotronic ZnO bicrystals, which benefit from a (0001)//(0001) alignment regarding the piezoelectric polarization vector, but simultaneously are disadvantageous when considering the dopant segregation in case of coherent (0001) inversion boundaries. Previous work on ZnO bicrystals clearly showed that grain boundary incoherency is an important parameter determining the segregation of large, normally insoluble elements such as praseodymium or bismuth to the interface. However, this immanent problem of the (0001)//(0001) orientation is solved by this specific synthesis route and hence both the piezoelectric response and the nonlinear current voltage (I V) characteristics were optimized. An enrichment of bismuth throughout the entire interface was achieved without the need to deviate from the specified alignment (Figure 1). The findings were successfully cross checked with a reference sample being diffusion bonded with the identical orientation but without the presence of a dislocation network along the bicrystal interface.

P. Keil, M. Trapp, N. Novak, T. Frömling, H. J. Kleebe, J. Rödel,
Piezotronic Tuning of Potential Barriers in ZnO Bicrystals
Adv. Mater., 30 [10] (2018) 1705573.

Keywords: ZnO varistors, Bicrystal Microstructure, SEM and TEM



ABS 892

ENHANCED THERMAL STABILITY IN QUENCHED LEAD-FREE $(1-x)(Na_{1/2}Bi_{1/2})TiO_3$-$xBaTiO_3$ PIEZOCERAMICS

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The driving force for innovation in lead-free piezoelectrics is the impending regulation (in 2021) that limits the use of lead in applications and demands to find avenues to replace the widely used lead zirconate titanate (PZT) [1]. Active research in the past two decades has already paved way to alternative material systems that can replace PZT in specific applications [2]. Among the several lead-free material classes, relaxor (1-x)(Na1/2Bi1/2)TiO3-xBaTiO3 (NBT-xBT) solid solution has been identified as a potential candidate for high-power applications [1]. The optimized piezoelectric properties are achieved at the Morphotropic Phase Boundary (MPB). For example, the MPB composition NBT-6BT exhibits a piezoelectric coefficient, d33, of 125pC/N and depolarization temperature, Td, of 100°C (the temperature at which the piezoelectricity vanishes). The limitation due to lower Td has been addressed in the past by chemical doping, a commonly adopted route to tailor the functional properties of PZT.

Quenching is not of major interest in the field of ceramics due to the thermally-initiated stresses leading to micro-cracking and failure. Nevertheless, quenching from above the critical phase transition temperatures has been explored in the realm of functional ceramics [3,4]. In this work, quenching is demonstrated as an alternative route to tailor the functional properties of piezoceramics. A comparative study is presented between quenched and furnace cooled NBT-xBT [5]. The microstructures of the quenched and furnace cooled samples are compared. It is established that Td increases by 40–60°C in quenched NBT-xBT compositions (see Figure). Annealing in oxygen atmosphere is shown to revert the Td back to that of furnace cooled samples. Temperature- and frequency-dependent permittivity and strain-field hysteresis ascertain the premise of stabilization of ferroelectric order in these compositions. Impedance spectroscopy results are used to comprehend the influence of quenching-induced defect concentration on the enhanced thermal stability in quenched samples. A systematic study of quenching from different temperatures is presented and the critical temperature limits are identified by tracking the thermal depolarization behavior.

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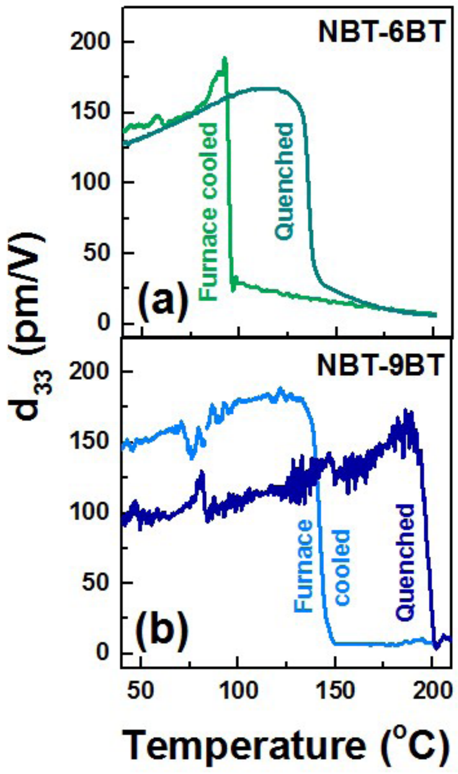
Keywords: lead-free piezoceramics, relaxors, quenching



ABS 891

ENHANCED ELECTROMECHANICAL RESPONSE IN RARE-EARTH-SUBSTITUTED $Bi_4Ti_3O_{12}$-$BiFeO_3$ PIEZOELECTRIC CERAMICS

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The attention of researchers to the high Curie temperature bismuth layered structure ferroelectrics (BLSF) is intensive but the materials do not have polarizations at a level desirable for device applications. The effect of rare earth ions substitution for bismuth was studied and significant improvements, in both the ferroelectric and piezoelectric properties, in Bi4Ti3O12 – BiFeO3 system have been achieved.

The reported investigations provides a consistent set of structural, ferroelectric and piezoelectric properties of samarium, gadolinium and dysprosium doped Bi4Ti3O12 – BiFeO3 ceramics and its comparative analysis to undoped material.

The morphological characterization shows micrograins with no visible defects. Unit cell parameter refinement and chemical analysis confirmed the proper material structure and composition. The electrical measurements of obtained ceramics is provided, by determination of the impedance parameters in the temperature range from 300 to 1000 K. The electric permittivity values at room temperature are in the range from 50 to 500 and shows strong frequency dependence. The corresponding loss factors exhibit a similar trend upon heating and its values are between 0.01 and 1. Finally it is recorded, that the most effective in increasing the value of piezoelectric coefficients is dysprosium substitution

Keywords: Multiferroics, Piezoelectric materials

ABS 889

PREPARATION OF TRANSPARENT/TRANSLUCENT SPINEL–BASED PHOSPHORS

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Preparation and characterisation of transparent spinel ceramics doped with both transition and rare-earth metals will be presented. A systematic study was performed to develop a processing methodology for elimination of microstructural defects in sintered samples and improving optical transparency. The powder was dispersed in a distilled water using Darvan C-N surfactant. Soft spinel granules with improved compressibility were made by freeze granulation. Green compacts were prepared by CIP-ing under 400 MPa pressure. Spinel specimens with relative densities >99.9% of theoretical were made by pressureless sintering in air at 1550 °C and subsequent HIP-ing at 1550 °C for 5 h in 200 MPa Ar gas. The optical real in-line transmittance (RIT) of polished spinel specimens was 95% of the theoretical at the wavelength range of 425-705 nm.

A series of translucent spinel $MgAl_2O_4$ phosphors doped with different cations were prepared. The $MgAl_2O_4$:Eu, $MgAl_2O_4$:Ce, $MgAl_2O_4$:Yb and $MgAl_2O_4$:Er phosphors emitted blue (460 nm), yellow (570 nm), blue-red (465 nm, 665 nm) and violet-red (427, 637, 684, 745 nm) light, respectively. Some of the phosphors excited by green light emitted dark-red light (715-720 nm).

This work was supported by SASPRO 1329/03/02-b, APVV-14-0385 and VEGA2/0164/18 projects.

Keywords: spinel, MgAlON, phosphors

ABS 887

PREPARATION OF Ce^{3+} AND Eu^{2+} ACTIVATED CERAMIC PHOSPHORS BY PRESSURE-LESS SINTERING

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Compared with single crystals, glass and glass ceramics, etc., ceramic phosphors turned out to be the most promising all-inorganic light converting material for high luminous density semiconductor light sources, which may have important applications in digital projectors and out-door illumination. Usually, ceramic phosphors were fabricated via vacuum sintering, spark plasma sintering, or hot pressing, etc., which need expensive sintering facilities. Here, we presented the sintering of Ce3+ and Eu2+ activated ceramic phosphors by a facile and cost-effective methods, that is, obtaining dense ceramic phosphors under atmospheric pressure in a tube furnace. The effects of gas environment and sintering aids, etc., on the densificaion of ceramic phosphors were disclosed. In addition, the influence of micro-structure, such as pores and secondary phases on the light extraction efficiency and light intensity homogeneity of the ceramic phosphors was discussed.

Keywords: ceramic phosphors,Ce3+,Eu2+

ABS 407

IMPROVED MICROSTRUCTURE AND FERROELECTRIC PROPERTIES IN B-SITE TI^{4+}-SUBSTITUTED $(BI_{0.86}Sm_{0.14})FeO_3$ POLYCRYSTALLINE CERAMICS

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In recent years, Bi0.86Sm0.14FeO3 has gained particular research interest since it exhibits morphotropic phase boundary (MPB) to which maximal electromechanical responses are expected. Interestingly, B-site Ti4+-doping in bismuth ferrite (BFO) based materials is expected to improve further the dielectric and ferroelectric properties by improving resistivity and stability of phase coexistence. In this work, the effects of Ti4+ doping (0.5% and 1%) in Bi0.86Sm0.14FeO3 are explored in terms of its microstructure, dielectric, piezoelectric, and ferroelectric properties in order for it be considered for applications in modern multistate memory elements, sensors, and spintronic devices.

Multiferroic (Bi_0.86 Sm_0.14)(Fe_(1-x) Ti_x) O_3 ceramics (BFO14Sm100xTi) for x=0.00,0.005,and 0.010 were synthesized using solid-state reaction method. Structural analysis was carried out using in situ X-ray diffraction (XRD), temperature-dependent in situ high-resolution synchrotron XRD (HR-XRD) and Rietveld refinements. Morphologies of as-sintered ceramics were obtained using a scanning electron microscope. Wayne-Kerr Analyzer PMA3260A was used to obtain dielectric permittivity at zero-field heating and cooling. Direct piezoelectric coefficients d_33 were measured using ZJ-6B piezometer at various dc poling electric fields. Polarization versus electric field (P–E) hysteresis loops were studied using Sawyer-Tower circuit at f = 46 Hz.

Scanning electron micrographs reveal that the Ti4+ doping facilitates slow oxygen ion diffusion leading to reduced grain size (2.13, 1.75, and 1.50 µm for BFO14Sm, BFO14Sm0.5Ti, and BFO14Sm1Ti, respectively). HR-XRD analysis and Rietveld refinements confirm the phase coexistence of polar R3c rhombohedral and nonpolar PbZrO3-like Pbam orthorhombic phases. The temperature dependent HR-XRD shows that the Ti4+ ions stabilize phase coexistence up to 250 °C. The enhanced dielectric homogeneity and decreased conductivity are caused by Ti4+ substitution, which are attributed to reduction of oxygen vacancies. The maximal piezoelectric coefficients (d_33) obtained at 100 kV/cm are 43, 51, and 53 pC/N for BFO14Sm, BFO14Sm0.5Ti, and BFO14Sm1Ti, respectively. The improved d33 and symmetric P–E hysteresis loops of BFO14Sm0.5Ti and BFO14Sm1Ti indicate enhanced ferroelectric order due to Ti4+ ion doping.

This work suggests that the Ti4+ doping could result in phase coexistence stabilization and effective enhancement of dielectric and ferroelectric properties in BFO multiferroics, which are important for practical applications.

Keywords: morphotropic phase boundary, dielectric homogeneity, ferroelectric order

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TEMPLATED GRAIN GROWTH OF [001]-ORIENTED LEAD ZIRCONATE TITANATE

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Successful Templated Grain Growth (TGG) of [001]-oriented Lead Zirconate Titanate (PZT) using anisometric (001) BaTiO3 (BT) templates is presented and the processing parameters critical to texturing PZT explored. PZT is a major piezoelectric material, widely used in industry, which exhibits good piezoelectric coefficients (d33, d31, ...), large coercive field (Ec), and high Curie temperature (Tc). Nanoscale PZT powder was mixed with 5 wt.% lead oxide (PbO) to act as a transient liquid phase and to promote epitaxy. Anisometric (001) BT platelet shaped seed crystals are mixed into a PZT slurry and oriented by tape casting. The tape is sectioned, stacked, and pressed into a green prior to binder burnout. During sintering, [001] oriented PZT grains nucleate on the (001) surface of the aligned BT templates and grow at the expense of the finer matrix material via Ostwald ripening. The resulting multilayer exhibits a texture in the [001] direction. PZT multilayers synthesized with 5 vol.% BT templates and 5 wt.% PbO show a Lotgering factor (LF) = 0.94, indicating near complete texturisation. Commercial 5A1 PZT variants were also successfully textured with a LF = 0.86. Large platelet-shaped pores at the BT-PZT matrix interface indicate that the templates are not stable within the PZT matrix. Large grain growth was observed in samples sintered for up to 8 h. Both the addition of PbO and nanoscale matrix particle size are shown to be critical in enabling the TGG of PZT.

Keywords: Lead Zirconate Titanate, Templated Grain Growth, Multilayers

ABS 885

TEXTURATION OF LEAD-FREE $BaTiO_3$ BASED PIEZOELECTRIC CERAMICS

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Piezoelectric ceramics have been integrated for a long time in a wide range of devices, particularly in ultrasonic applications (sonar systems, medical imaging…) and most of them use Pb(Zr,Ti)O3 (PZT) materials. However, due to health care and environmental problems, lead content must be reduced in such applications [1]. Among the few lead-free materials families which can be considered for the replacement of PZT [2, 3], BaTiO3 appear as interesting because of its piezoelectric properties at room temperature and capacity to be modulated by doping, even if Curie temperature is not very high (120°C).
However, ceramics are generally limited by their isotropic nature. For this reason, texturing process was developed in order to improve/optimize their electromechanical properties. The aim of the present study is thus to obtain textured BaTiO3 based materials by using the templated grain growth process (TGG) and to measure their piezoelectric properties.
Doped and undoped BaTiO3 powders were prepared by classical solid state route while BaTiO3 templates were elaborated by a molten salts process. Green ceramics were then obtained by tapecasting of a slurry containing templates and matrix particles dispersed in the appropriated solvent. After drying, green sheet was cut, stacked, pressed and then sintered at the appropriated temperature, in order to obtain thick or thin samples. This process allowed obtaining highly-oriented materials (texturation degree 70% to 90%). Piezoelectric properties were investigated, for doped and undoped samples, and for different sintering parameters. Some samples appears as very interesting for piezoelectric applications with d33* higher than 300 pC/N, against 180 pC/N for BaTiO3 ceramics obtained by classical way.

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Keywords: Lead-free ceramics,texturation,piezoelectric materials

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AMMONIA SELECTIVE SENSORS BASED ON COBALT SPINEL PREPARED BY SOLUTION COMBUSTION SYNTHESIS

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Ammonia is a primary eye and upper respiratory tract irritant, principally generated when manufacturing nitrogenous fertilizers and other chemical substances. Thus, this gas is nowadays also widely used as a refrigerant. The Time-Weighted Average for ammonia over 8 h should not exceed 25 ppmv and the short-term exposure over 15 min is limited to 25–35 ppmv. Therefore, it appears necessary to develop ammonia sensors able to detect this gas in the range of aforementioned concentrations. Gas sensors based on metal oxide semiconductors seem suitable for this purpose. Especially Co3O4, a well known p-type semiconductor with a good catalytic activity for the oxidation of reducing gases, could be a good candidate. However, up to now it has not been widely investigated for ammonia gas detection at ppmv level and this is the aim of this work.

The Co3O4 powder was synthesized by a Solution Combustion Synthesis route, using glycine as fuel and cobalt nitrate hexahydrate as a cobalt precursor and oxidizer. Afterwards, the powder was calcined in static air to remove all by-products and then fully characterized. Sensors were prepared by screen-printing the powder onto alpha-alumina substrates with platinum interdigitated electrodes. The sensors were dried overnight and fired in oven, then tested in a homemade gas-testing system.

The formation of the cubic Co3O4 phase was evaluated and confirmed by XRD and XPS observations. By applying the Scherrer equation, the crystallite size was find to be equal to 58 nm. FESEM observations were also performed and evidenced that the powder was made by nanocrystals with a rombicuboctahedral shape. From TEM observations, particles were in the range from 20 nm to 60 nm, in good accordance with FESEM analysis.TG-DSC, laser diffraction granulometry, HR-TEM, B.E.T., Raman spectroscopy, H2 temperature programmed reduction and H2O adsorption were also carried out.

The sensors were first tested toward 50 ppmv of ammonia at different temperatures, for evaluating the optimum working temperature that was find to be 225 °C. Then, different ammonia concentrations between 1 and 50 ppmv were investigated at this temperature. The sensors response was almost linear with increasing ammonia concentration, reaching a maximum value of 1.83 at 50 ppmv. The sensors response and recovery times so did the sensitivity were reasonable for the proposed application (60 s, 396 s and 0.0147 ppmv-1 respectively at 225 °C).Cross-sensitivity tests toward humidity, CH4, O3, and CO2 and CO highlighted no interferences, except with humidity.

Keywords: Gas Sensors,MOS,Co3O4

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EFFECT OF MICROSTRUCTURE ON THE IONIC TRANSPORT OF MAGNESIA-DOPED PSZ

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The great thermal shock resistance of magnesia partially stabilized zirconia (Mg-PSZ) makes this material suitable for various engineering solutions, such as thermal barrier coatings or disposable oxygen sensors. The presence of three crystalline phases (monoclinic (M), tetragonal (T) and cubic (C)), as well as the respective content and the 3D arrangement of each phase are determinant on the properties of these materials. The microstructure is featured by needle like formations, M and/or T and large C grains. The size of these formations may vary between nano and micrometric. The yet controversial effect of microstructure on ionic transport is the main subject of the present work. In fact, the complex chemical composition – processing – microstructure - property relationships in these materials prevent an easy discrimination of relevant parameters determining ionic transport. Interestingly, even reported roles of composition on ionic transport seem highly controversial, as opposed to common reports on other fluorite-based oxide-ion conductors (e.g., ceria-based).

Various microstructures were obtained from several standard Mg-PSZ materials (5-10 MgO mol% range), sintered at 1700 °C, but experiencing slight variations on the cooling profile. The materials were firstly characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and dilatometric thermal analysis (DIL). The electrical properties were addressed using impedance spectroscopy technique (IS), in air, with temperature ranging between 500 and 800 °C.

Combined microstructural analysis (SEM) and phase quantification (XRD) demonstrated the complex relations between phase content and microstructure, while changing only the cooling profile. The microstructure is clearly related to the observed thermal expansion (DIL) and electrical properties (IS). Significant departures from linear volume changes observed by DIL on heating revealed different stages of the transformation of M particles into T. Attempts are made to relate the variation of the distribution and size of needle like formations with the total conductivity of these materials. The detrimental segregation of magnesia to the grain boundaries, as a consequence of the transformation of the T into the M phase, with decreasing MgO solubility limits (predicted in the phase diagram of the system), may be avoided adjusting the cooling profile.

Acknowledgements

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Keywords: Mg-PSZ, Microstructure, Ionic transport, Phase content

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EVALUATION OF A MULTI-PURPOSE MEASUREMENT CELL FOR STANDARDIZED VOLUME RESISTIVITY MEASUREMENTS AT HIGH TEMPERATURES

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The ProboStat® is a multi-purpose measurement cell suitable for various electrical and physical measurements under different atmospheres and at high temperatures. Disc and bar shaped samples are sandwiched between platinum electrodes at the top of the tubular cell. The gas tight assembly can be inserted into a furnace. Different gases can be flushed through the tube. For this study, a ProboStat® was adapted to measure volume resistivity of ceramic insulators at high temperatures according to standards.
The standardized measurement of volume resistivity of ceramic insulators requires the consideration of many specifications including sample diameter, thickness, electrode design, and the proportion of these characteristics. Measurements are ideally performed in a state of dielectric equilibrium. The time-related slope of resistivity of a specific sample follows a power function. Thus, care must be taken when choosing a charge time or defining the duration of a measurement. As fringing of the guarded electrode occurs under high voltage, the effective electrode area for evaluation of the results should be corrected with respect to sample thickness and electrode design. The demands of effective standards on sample geometry and electrode design are stricter for room temperature measurements than for high temperature measurements.
To perform high temperature measurements on ceramic samples that also fulfill the demands on room temperature measurements, a ProboStat® was equipped with a dedicated large sample setup for discs with diameters of up to 60 mm. The volume resistivity of different alumina samples was first measured at room temperature in a standard test fixture and then compared to results obtained with the ProboStat®. All measurements were performed for at least 100 min using a 26 mm guarded electrode. High temperature measurements at 500 °C were performed using the same samples. Room temperature values obtained with the standard test fixture are in the order of 10^17 Ohm·cm. The quantitative effect of electrode area correction is presented. Practical issues related to the use of the multi-purpose cell are addressed. These include electrode material selection, application of electrodes, and compensation of leakage currents. High temperature results of volume resistivity of the different alumina samples are presented. The validity is discussed with respect to the suitability of the multi-purpose cell for such measurements.

Keywords: volume resistivity, alumina, high-temperature

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$BaTiO_3$-CERAMICS ELECTRORESISTIVITY AND HAYWANG INTERGRANULAR CAPACITY FRACTALS MODEL

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BaTiO3-ceramics is very well known electroceramics material and has a more than 300, now a days, very advanced applications. The atomic structures packed by Euclidian geometry, up to the nano sizes, are not suitable for particles flows and irregular structures. In order to analyze more originally these structures, apply fractal nature approach. There is existing trend in the now a days literature that a wide range of disordered systems can be characterized by the fractal nature over a microscopic correlation length. The modern ceramics science, faces with very important priorities of the future frontiers which opens new directions within higher knowledge structure even down to nano and due to lack of energy, towards new and alternative energy sources. There is a fact, that energy transformations are permitted on a small scale. Through our actual research we recognize that BaTiO3 and other electronics ceramics have fractal configuration nature based on three phenomena. Ceramic grains have fractal shape seeing as a contour in cross section or as a surface; the other one phenomena is related to so called “negative space” made of pores and inter-granular space. The porosity is extremely complex and has very important role in microelectronics, micro-capacity, PTC, piezoelectric and other phenomena. The third, there is Brownian process of fractal motions inside the material, during and after sintering, in the form of micro-particles flow (ions, atoms and electrons). These is important phenomenology based on inter-granular micro-capacity and super micro-capacitors in function of higher energy harvesting and storage. Fractal nature theory allows recognizing micro-capacitors with fractal electrodes. The method is based on iterative process which is compatible with the grains and pores model. In this paper, based on fractals corrected Heywang model, we analyse the electroresistivity as a part of intergranular micro-impedance. Also, we successfully applied the complex fractal correction on thermodynamic parameters, especially the temperature. On this way we continue to open the new fractal nature frontiers within the electro parameters, like elastoresistivity.

Keywords: ceramics, intergranular resistivity, fractals

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ANTI-POLAR ORDER IN TETRAGONAL TUNGSTEN BRONZE $K_2RNb_5O_{15}$ (R: RARE EARTH)

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The dielectric constant of ferroelectric BaTiO3, which has been widely used as a base material for multilayer ceramic capacitors (MLCC), drastically decreases under a high electric (E) field due to the saturation of electric polarization. This motivates us to search for a new candidate of antiferroelectric (AFE) material, where the dielectric constant increases under an E-field due to a phase transition to the ferroelectric state. However, the current candidates of AFE materials are mostly limited to the lead-containing perovskites. Here, we focus on a new class of lead-free AFE materials based on K2RNb5O15 (R: rare earth) with tetragonal tungsten bronze (TTB) structure (ref. 1).

MLCC samples with Pt-inner electrodes, where the effective area and thickness of the dielectric layer are ~ 3 mm2 and 48 µm, respectively, were prepared by conventional solid state reaction and the existing MLCC processes. The crystalline phases were analyzed by X-ray diffraction and transmission electron microscopy. Electric polarization and dielectric constant under an E-field were measured with a ferroelectric tester and an LCR meter. Density functional theory (DFT) lattice dynamics calculations were also carried out to elucidate the stable polar and anti-polar crystal structures.

The highly insulating samples were successfully obtained by optimizations of chemical composition and fabrication processes. Clear double hysteresis loops and corresponding peaks in E-dependence of dielectric constant, which are typical for AFE, were observed in K2PrNb5O15. The temperature dependence of dielectric constant also insists the successive phase transitions from ferro- to antiferro-, and to paraelectric. Our DFT calculations reveal new structural phases of TTB with an AFE order which are energetically comparable to the conventional ferro- or paraelectric phases. These results are well-consistent with the successive phase transitions.

Phase transitions and the formation of anti-polar crystal structure (AFE phase) in K2RNb5O15 are demonstrated by both experimental and theoretical results. The dielectric property of K2RNb5O15 under an E-field is similar to conventional AFEs such as (Pb,La)(Zr,Ti)O3 and Pb(Sn,Ti)O3. Since there have been only a few candidates of lead-free AFE, this work will open up a new avenue for lead-free AFE and its capacitor applications.

1. Y. Gagou et al., Journal of Applied Physics 115, 064104 (2014).

Keywords: antiferroelectric, lead-free, tetragonal tungsten bronze

ABS 949

INFLUENCE OF Ba^{2+} ADDITION ON STRUCTURE AND FUNCTIONAL PROPERTIES OF $Bi_{0.5}Na_{0.5}TiO_3$ PIEZOCERAMICS

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Fossil fuels are playing a dominant role in global energy systems, but they are also the main contributors of air pollution and greenhouse effect. Due to trend to replace fossil fuels with new and green energy sources, piezoelectric energy harvesting is attracting a lot of attention recent years. Piezoelectric materials have an ability to transform mechanical energy, usually ambient vibrations, movements or stress into electrical energy (and vice versa) that can be stored and used to power other devices. Lead-free materials with perovskite structure such as bismuth sodium titanate (Bi0.5Na0.5TiO3) based materials are one of the promising candidates to replace toxic lead-based materials, due to their excellent piezoelectric properties. Bismuth sodium titanate (Bi0.5Na0.5TiO3) modified with barium titanate (BaTiO3) powders were synthesized by a hydrothermal method in alkaline environment. Bismuth nitrate (Bi(NO3)3•5H2O), barium nitrate (Ba(NO3)2), titanium (IV) butoxide (C16H36O4Ti) and sodium hydroxide (NaOH) were used as starting materials. Aqueous solutions, with different amount of Ba2+ (up to 10 at.%) were hydrothermally treated in autoclave at pressure of 7 bar for 6 hours. The synthesized powders samples were dried, pressed into pellets and finally sintered at different temperatures up to 1200 °C in order to obtain dense ceramics. The aim of this work was to investigate influence of Ba2+ addition and different processing parameters on the structure and functional properties of Bi0.5Na0.5TiO3. Structure of the prepared samples was analyzed by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy, while dielectric, piezoelectric and ferroelectric measurements were used for functional characterization.

Keywords: piezoelectric, bismuth sodium titanate, lead-free

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MICROWAVE SINTERING: IMPROVEMENT OF THE ELECTRICAL PROPERTIES OF BARIUM TITANATE DOPED WITH CALCIUM AND ZIRCONIA

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Objective Lead based piezoelectric ceramics are used in many applications (sensor, transducer, …), especially Pb(Ti,Zr)O3 (PZT). The scientist community focused on lead-free piezoelectric ceramics because the toxicity of lead has been demonstrated and the European legislations (REACH, RoHS, WEEE) advocates the removal of toxic elements in the advanced materials. For low temperature applications, barium titanate doped with calcium and zirconia has been studying for 10 years and could be a promising candidate to replace PZT based material. For pure barium titanate, some studies demonstrate the benefit of the microwave sintering. The aim of the present work is to study the influence of the micro-wave sintering on the electrical properties of Ba0.85Ca0.15Ti0.90Zr0.10O3

Materials & Methods Ba0.85Ca0.15Ti0.90Zr0.10O3 was prepared by conventional solid-state route using BaCO3, CaCO3, TiO2, ZrO2 as starting materials. These powders were mixed in stoichiometric ratio by attrition milling in alcoholic media. The slurry was dried and conventionally calcined at 1300°C during 2 hours. The calcined powder was ball milled by attrition in alcoholic media. The ball milled powder was compacted into pellets by uniaxial pressing followed by cold isostatic pressure. The samples were sintered by two sintering methods: conventional and microwave sintering.

Results Different dwell time sintering, from 5 minutes to 60 minutes, have been tested. The electrical properties, the grain sizes, and the crystalline structures were measured for each sample and compared to samples sintered by conventional method. Electromechanical behavior has been also investigated at the local scale by piezoresponse force microscopy.

A finer microstructure can be observed for sample sintered by microwave sintering due to the used short times and materials are densified more than 94% of the theoretical density.

If samples are densified during 40 minutes by microwave, better electrical (e.g piezoelectric) properties are observed compared to conventional sintered ones.

Conclusions It was shown microwave sintering is benefical for the piezoelectric properties. Moreover, the sintering time is drastically reduced (Maximum 1h30 for microwave sintering against 12h30 for conventional sintering).

Keywords: Microwave sinterng, Lead free piezoceramics, Electrical characterizations

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ATOMIC RESOLUTION STEM IMAGING OF RARE-EARTH DOPANT NANOCLUSTERS IN LONG AFTERGLOW STRONTIUM ALUMINATE PHOSPHORS

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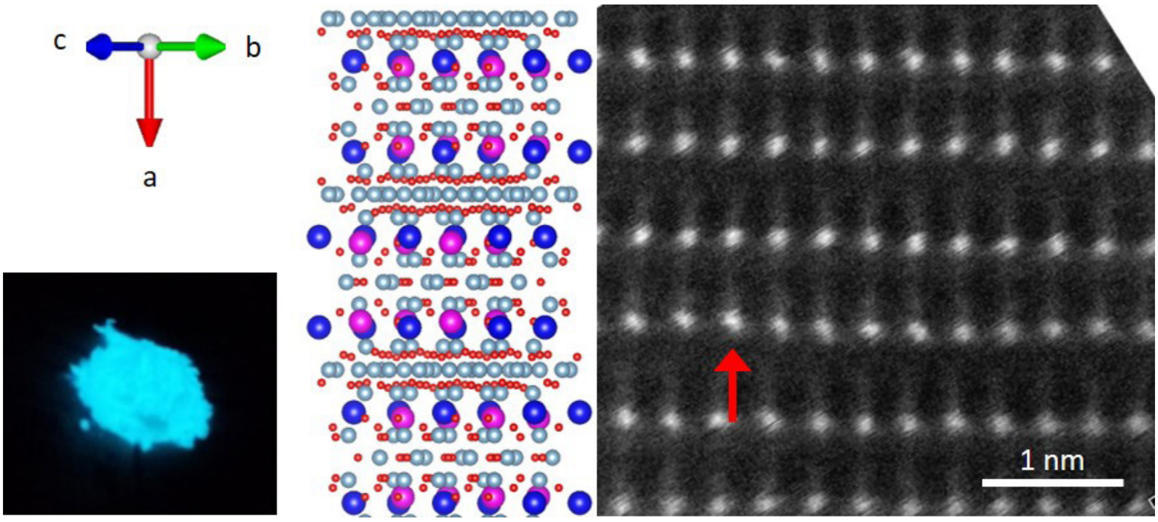
Ceramic pigments emitting long afterglow have enormous potential for lighting applications that consume zero energy from the power grid. One of the most efficient energy-storing pigments is strontium aluminate, when co-doped with 2 rare-earth elements—an optically active emitter, such as Eu, and an auxiliary ion, such as Dy. To date, spectrophotometric methods are commonly used to determine the material structure supporting long afterglow, yielding indirect evidence of energy transfer between the rare-earth co-dopants. Here, using atomic resolution HAADF-STEM imaging, distinct columns of Sr sub-lattice sites in the (012)-projection are resolved in a Sr4Al14O25:Eu,Dy single crystal. We show through quantitative STEM image simulations that substitutional incorporation of the rare earth dopants into Sr sites enhances the image contrast by 125% over that of neighboring atomic columns in boron-doped compounds. DFT structural simulations reveal that divalent Eu and trivalent Dy incorporate into adjacent Sr lattice sites along the [012], while WDS analyses indicate that an optimal concentration of rare-earth dopants is necessary for such clustering to occur. These results are observed in structures incorporating boron, suggesting that boron enables the dopant defect clustering that manifests as extremely long afterglow. Our approach reveals fundamental insight into the role of boron doping on material structure that supports extreme persistent luminescence in co-doped ceramic oxide compounds.

Keywords: extreme persistence, atomic resolution HAADF-STEM,DFT



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MULTICALORIC PROPERTIES OF (1-x)Pb($Fe_{0.5}Nb_{0.5}$)O_3-x$BiFeO_3$ SOLID SOLUTIONS

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Most of the current activity in the research of alternative cooling technologies is oriented towards one of the caloric effects, either electrocaloric (EC), magnetocaloric (MC) or mechanocaloric, where the entropy of the material and thus its temperature changes under the application of external stimuli, i.e., electric, magnetic or mechanical (stress), respectively [1]. The interest has also recently increase for multicaloric materials, where the application of two or more stimuli (electric, magnetic or mechanical) can enhance the total caloric effect or extend the operating temperature range of cooling device [2].

The existence of EC and MC properties in the same material was already demonstrated in Pb(Fe0.5Nb0.5)O3 (PFN) ceramics [3]. While this material appears promising, it possesses a relatively small EC and MC temperature changes at room temperature (RT), i.e. ~0.8 K and ~2 mK, respectively. Additionally, a maximum value of MC effect remains at very low temperatures (2 K) and therefore further developments are needed. According to the literature, PFN-BFO solid solutions exhibit antiferromagnetic-paramagnetic phase transition in the vicinity of RT [4]. Since in general the highest caloric effects are obtained near ferroic phase transitions [1,5], it is expected that PFN-BFO solid solutions should exhibit higher MC effect with the maximal value close to the RT. At the same time, the addition of smaller amount of BFO (<50%) does not effect on ferroelectric-paraelectric phase transition [6], which remains slightly above the desired RT.

In order to find the composition with the highest multicaloric properties, four (1-x)Pb(Fe0.5Nb0.5)O3-xBiFeO3 (PFN-BFO, x = 0.05, 0.1, 0.2 and 0.5) solid-solutions are prepared by mechanochemical synthesis followed by sintering at the temperatures between 900 °C and 1000 °C. The EC and MC effects as well as electrical conductivity, dielectric and ferroelectric properties of the prepared PFN-BFO ceramics will be presented and discussed by comparing with the literature data. Additionally, the influence of the manganese doping on functional properties of PFN-BFO will be discussed.

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Keywords: Multiferroic, Electrocaloric, Magnetocaloric

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POLYMERIZABLE CERAMIC INK SYSTEM FOR THIN INKJET PRINTED DIELECTRIC LAYERS

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Since printed electronics have become an important research area in the last few years, there is a high interest in printed dielectric layers. These layers are amongst others needed for producing capacitors for several applications. To attain high capacities, materials with large permittivities are required, which have to be printed as thinly as possible. Ferroelectric ceramics show high permittivities in general, but are challenging to print by inkjet printing. Whenever diluted particulate ink systems are used, typical undesired drying effects can occur. To avoid these drying effects and to achieve thin layers (~ 1 µm) a reactive ceramic ink system for inkjet printing was developed. This innovative system contains surface modified Ba0.6Sr0.4TiO3 (BST) particles, a crosslinking agent, as well as a thermal radical initiator. The polymerization starts immediately after the ink drop contacts the heated substrate and therefore leads to very homogenous topographies. Since an organic/inorganic composite ink is used, no sintering is needed after printing and thus printing on flexible substrates is possible.

The BST particles are synthesized in a sol-gel process, the resulting gel is spray-dried and the received precursor is subsequently calcined at 1100 °C for two hours. The calcined powder is grinded in a stirred media mill with 200 µm ZrO2 milling beads until particle size is < 200 nm. Surface modification is carried out in two steps: First, BST particles are oxidized with a 30 wt.% solution of H2O2. Second step is a silanization with 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) in toluene, to generate a polymerizable group on the particle surface. The print-ready ink contains 5 vol.% modified BST, 5 vol.% Poly(ethylene glycol) diacrylate and a small amount of a thermal initiator, suspended in butyldiglycol/isopropanol.

A comparison between modified and non-modified BST with the described ink system is performed. To investigate the advantage of the surface modificated particles, topographies of different printed structures are compared by white light interferometry. The occurring polymerization is confirmed by measurements with an oscillatory rheometer. Layer thicknesses are determined by SEM images and the capacity is measured via impedance spectroscopy.

The process of thermal polymerization during printing enables the production of thin ceramic layers with very homogenous topographies, since undesired drying effects can be avoided. Thus, thin dielectric layers of about one µm with high ceramic content can be printed on flexible substrates. Furthermore, surface modification can be performed with a large variety of materials, enabling many different applications.

Keywords: inkjet printing, dielectric layer, polymerizable ceramics

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INFLUENCE OF CRYSTALLIZATION PROCESS PARAMETERS ON CRYSTALS GROWTH MECHANISMS, MICROSTRUCTURE AND PIEZOELECTRIC PROPERTIES OF GLASS-CERAMICS CONTAINING FRESNOITE CRYSTALS

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Objectives This work is part of a project that aims at developing high temperatures pressure Surface Acoustic Waves sensors. For that purpose, piezoelectric glass-ceramics containing fresnoite crystals have been developed and successfully tested up to 800°C. However, parent glass crystallization needs to be further studied in order to control the glass-ceramic microstructure and properties.

Materials and methods The glass-ceramic contains a crystalline pyroelectric and non-ferroelectric phase. Macroscopic piezoelectric properties are obtained if the crystallization leads to a preferential orientation of the crystal's polar axis (c-axis).
The parent-glass composition 2SrO-TiO2-3.3SiO2-0.1Al2O3-0.2K2O is obtained by mixing reagent-grade SrCO3, TiO2, SiO2, K2CO3 and Al2O3, followed by melting at 1500°C. The resulting glass ceramic is homogenous (70 vol% of fresnoite crystals and 30 vol% of residual glass).
Crystallization is performed by heating the parent glass plate up to a temperature ranging between 850°C – 950°C, for various plateaus.

Results For all temperatures, a surface nucleation mechanism leads to a crystallization front propagating from the surface into the bulk over time, with fronts junction after a suitable time (i.e. 15h at 900°C). Velocity of the front increases with temperature. XRD analyzes show a strong preferential orientation of (002) planes for low depth (<100 µm). Between 100 and 300 µm, a progressive tilt of the preferential orientation at the benefit of (201) planes is sometimes observed. This tilt does not seem to be related to the heat treatment temperature but may be due to the influence of the parent glass surface roughness and the material in contact with the glass. A mirror-polished glass specimen, embedded in a powder bed or between two substrates, were crystallized at 900°C. The crystallization front speed in the powder bed is twice slower than between substrates. Two different natures of powders and substrates were tested: alumina and zirconia of same grains size, and no influence on preferential orientation was highlighted. In addition, the velocity of the crystallization front is not related to the preferential orientation and it excludes the hypothesis of a plane's kinetic selection mechanism.

Conclusion The crystallization of this specific glass composition leads to a glass-ceramic composed of 70 vol% of Sr2TiSi2O8 crystals and 30 vol% of residual glass. For all tests, strong (002) planes preferential orientation is observed for low depth. After 100µm, a tilt to (201) planes is sometimes observed. However, its origin is not yet understood, and it was impossible to relate this tilt to processing conditions.

Keywords: Glass-ceramic, Surface crystallization, Piezoelectric

ABS 877

DIELECTRIC AND PIEZOELECTRIC NON-LINEARITIES: DECRYPTING ELECTRO-MECHANICAL COUPLING OF RELAXOR-FERROELECTRICS

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Ultra-high piezoelectric coefficients in perovskite relaxor-ferroelectrics, such as lead magnesium niobate titanate (PMN-PT), are commonly attributed to a polarization rotation mechanism in domain-engineered single crystals [1]. However, this rotation mechanism cannot explain the dielectric and piezoelectric anomalies in the cryogenic temperature range that are observed in a number of technologically-relevant relaxor-ferroelectrics [2]. These anomalies raise questions not only about their physical origin, but also about their contribution to the ultra-high piezoelectric coefficients of relaxor-ferroelectrics at ambient temperatures. Dielectric and piezoelectric non-linarites are related to underlying physical mechanisms [3]. In this work, we present an in-depth study of non-linearities in a variety of relaxor-ferroelectric single crystals in an attempt to decrypt electro-mechanical coupling. We measure and compare the dynamic strain and polarization response in the sub-coercive regime as a function of crystal orientation, driving field and frequency. In addition, sub- and super-coercive polarization measurements between 10 and 290 K are performed.

We clearly observe different non-linear strain and polarization responses along different crystallographic directions. These results will be used to discuss the evolution of dielectric non-linearities and anomalies in the cryogenic temperature range. To better understand the underlying mechanisms, these results will be compared to barium titanate and lead-free relaxor-ferroelectric single crystals.

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Keywords: piezoelectric, relaxor-ferroelectric, single crystal

ABS 246

SINTERING MECHANISM, DENSIFICATION AND EXAGGERATE GRAIN GROWTH IN CaCu3Ti4O12 CERAMICS

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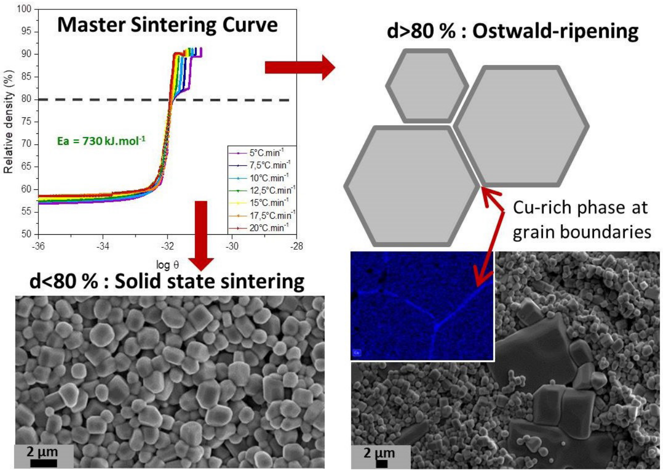
Context & Objectives In the last years, the research of materials having high dielectric constant with good temperature stability has raised significant attention because of their interest in many potential applications. Calcium copper titanate CaCu3Ti4O12 (CCTO) shows a very high relative dielectric permittivity (εr > 10^4), moderate dielectric losses (tanδ ~ 0.15) at 1 kHz over a wide range of temperatures from 100K to 400K with no phase transition. Shortly after the reports of those properties, the origin of the colossal dielectric constant has been questioned and arguments have been put forth that extrinsic effects may be the sources of this giant dielectric constant. In the case of polycrystalline materials, interfacial contributions have been put forward induced by semi-conducting grains and insulating grain boundaries. As the CCTO dielectric behavior is clearly linked to its microstructure, the aim of this proposal is to identify the sintering mechanism and to study the grain growth of CCTO during conventional sintering.

Materials & Methods For this purpose, dilatometric study was conducted in detail to find out which diffusion mechanism is responsible for densification. The Master Sintering Curve was also determined to predict and characterize the densification process of CCTO ceramics and to estimate the apparent sintering activation energy. Finally, structural and microstructural characterizations (X-Ray Diffraction, Energy-dispersive X-ray spectroscopy, Scanning and Transmission Electron Microscopy) have been realized.

Results Based on the shrinkage curves and linear shrinkage equations, it was shown that the dominant diffusion mechanism leading to densification during the initial stage of sintering is the grain boundary diffusion. For this mechanism, the apparent sintering activation energy, determined by using the MSC model, was found to be ~730 kJ.mol-1. The microstructure evolution of CCTO during conventional sintering was also studied through the sintering trajectory, which corresponds to a unique relationship between grain size and density. According to microstructural analysis, it was shown that abnormal grain growth takes place for samples sintered at high temperature stage with density > 80% of the theoretical density due to the presence of a Cu-rich liquid phase at grain boundaries.

Conclusion This work contributes to a better understanding of the sintering behavior of CaCu3Ti4O12. Thus, based on the densification mechanism and the origin of exaggerate grain growth in CCTO, the control of microstructures will be possible and will help to understand and tune dielectric properties.

Keywords: CaCu3Ti4O12,Sintering mechanism, Microstructure



ABS 875

$SrAl_2O_4$:Eu,Dy-SCREEN-PRINTED LAYERS TO CREATE PHOSPHORESCENT 2D SHAPES

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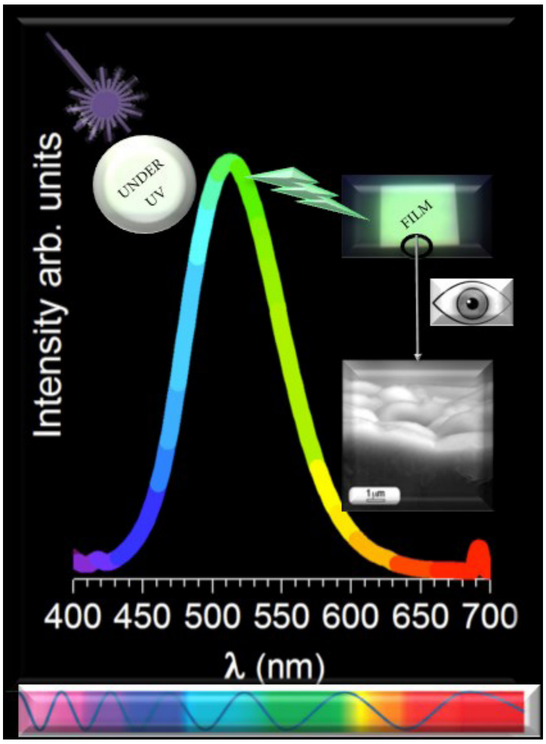
Among persistent luminescence materials, the SrO-Al2O3 system mainly with rare earths has been widely studied due to its chemical stability, high photoluminescence response and the longest green-afterglow time. This research has focused on SrAl2O4 doped with europium and dysprosium. Here we show a methodology to fabricate a versatile 2D planar designs based on the SrAl2O4 system for a high-performance photoluminescence (PL) response by reactive screen-printing methodology.Versatile ink compositions incorporate the reactive precursor to promote textured SrAl2O4:Eu, Dy films during the thermal treatment. The novelty of the approach is that we can tailor the phosphorescent response by the reactivity of the ink precursors. The ink is formulated and printed onto substrate in a single step. The study shown that both the treatment temperature and the substrate nature contributed to the improvement of the photoluminescence response, meanwhile, the appearance of secondary phases promoted the photoluminescence reduction. The emission intensity of SrAl2O4 phase increased with the texturing. Our results will help to understand and facilitate the development of luminescent films through a screen-printing technology that gives the possibility of producing layers with low cost and easily scalable processes.

Keywords: photoluminescence,screen-printing,SrAl2O4



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EFFECT OF PHASE TRANSITION AND ORBITAL HYBRIDIZATION ON DIELECTRIC AND FERROELECTRIC PROPERTIES OF BARIUM ZIRCONATE TITANATE CERAMICS

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Objectives Lead-free Zr-doped barium titanate (BZT) materials have been studied extensively for dynamic RAMs, multilayer ceramic capacitors and tunable microwave devices due to their superior dielectric and ferroelectric properties. Phase coexistence and ferroelectric to relaxor transition near the materials' invariant critical point (ICP at Zr = 15%) and degree of orbital hybridization seem to play a critical role in enhancement of these properties. This study aims to provide insightful correlation between dielectric properties and orbital hybridization of BZT near ICP to aid further development of BZT for commercial purposes.

Materials and Methods Polycrystalline Ba (Zr_yTi_(1-y))O_3 (BZT) (y = 0.10, 0.15 and 0.20) ceramics are synthesized using conventional solid-state reaction method. Grain morphologies were obtained using a Hitachi S-3400N scanning electron microscope (SEM). X-ray diffraction (XRD) spectra from Rigaku Multiplex Diffractometer, Rietveld refinement with HighScore Plus software and high-field transmission electron microscope (HRTEM, JEOL JEM-2100) were used for structural analysis. Wayne-Kerr Analyzer was used for dielectric permittivity measurements while a Sawyer-Tower circuit was used for polarization versus electric field (P-E) hysteresis loops. O K-edge and Ti L-edge synchrotron X-ray absorption spectroscopy (XAS) was performed in transmission mode at the 01C1 beam line of the National Synchrotron Research Center (NSRRC) in Taiwan.

Results Rietveld refinement and TEM diffraction patterns shows structural change from tetragonal to cubic phase as Zr-doping concentration increases with P4mm (12.4%) and Pm3m (87.6%) phase coexistence at ICP. Dielectric permittivity measurements reveal Zr-induced relaxor behavior as doping concentration increased due to decrease in O 2p-Ti 3d orbital hybridization. Highest permittivity is achieved at 0.15mol% Zr (ε'=7259.49) which may be attributed to the increase of orbital hybridization and phase coexistence. Phase coexistence near ICP increases number of available polar states lowering energy barrier for polarization changes. Increase in O 2p-Ti 3d orbital hybridization lowers energy making it easier to induce switching between the different states in the system. Lower remanent polarization (P_r) values at ICP may be attributed to reduction of polar long range order as non-polar Pm3m phase dominates.

Conclusion Increased O 2p-Ti 3d orbital hybridization and phase coexistence at ICP contributes significantly to enhanced dielectric permittivity in BZT which makes these systems potential for energy conversion applications.

Keywords: orbital hybridization, phase coexistence, dielectric permittivity

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FRACTURE BEHAVIOR OF LEAD-FREE KNN PIEZOELECTRIC CERAMICS

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Multilayer actuators suffer severe strain incompatibility at electrode edges and therefore require succinct knowledge of crack resistance of new lead-free piezoceramics. To this end, the fracture toughness of lead-free KNN piezoelectric ceramics with composition of 0.92KNN-0.02Bi0.5Li0.5TiO3-0.06BaZrO3 was investigated. To get a comprehensive assessment, the intrinsic fracture toughness (K_IO), as well as the fracture toughness of short and long cracks were evaluated by using the near-tip crack opening displacement (COD) method, the surface crack in flexure (SCF) method, and the single edge V-notch beam (SEVNB) method, respectively. At room temperature, the K_IO, evaluated by the COD method, was lowest, with a value about 0.70 MPam0.5, demonstrating domain switching or phase transition happened and induced toughening during crack propagation in KNN. K_Ic, measured by the SEVNB method, was highest, with a value of about 1.0 MPam0.5. Intermediate fracture toughness, at about 0.90 MPam0.5, was obtained by the SCF technique. The difference of values can be rationalized by taking the effect of crack geometry between the SCF and SEVNB method, combined with the toughening behavior of the material, into consideration. With increasing temperature the degree of toughening diminshed. At 180oC and 350oC, the fracture toughness values measured by the SCF and SEVNB method are nearly equal with each other, suggesting an absence of toughening by domain switching. The disappearance of the toughening at 180oC and 350oC can be rationalized by the very small remanent strain from the stress-strain curves measured during mechanical compression, with values of 0.015% and 0.003%, respectively. As linear stress distribution was assumed for the establishment of the equations for the calculation of the fracture toughness in the SCF method, the nonlinear behavior of KNN during four point bending was also evaluated using strain gauge techniques. Further analyzes demonstrated that the fracture toughness is overestimated by about 2% if the linear stress distribution in the bend bar is assumed.

Keywords: fracture toughness, domain switching, lead-free piezoceramics

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DEFECTIVE CERIA ACTUATOR: THE INFLUENCE OF ELECTRODES.

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The discovery of electrostriction in gadolinium-doped ceria ($Ce_{1-x}Gd_xO_{2-\delta}$, (CGO)) [1] drew great interest in recent years as a promising candidate for a new generation of electromechanical actuators displaying high performances comparable to the traditional PZT materials, i.e. Q= 20-80 m^4/C^2 [2] and Q= 0,02 m^4/C^2 [3] for CGO and $Pb(Mg_{1/3}Nb_{2/3})O_3$ respectively. Furthermore, CGO is an environmental friendly material, which do not include lead (Pb) and is compatible with Si technology.

In this work, we study the performances and stability of CGO thin films growth by pulsed laser deposition (PLD), in particular using TiN ceramic electrodes. Such fabrication technique enables control of microstructural features of CGO and resulted in several advantages such as high performances (Q= 40 m^4/C^2), enhanced mechanical coupling and higher stability. A ceramic electrode is necessary in order to avoids electrodes detachment or oxidation layer that form often when using metals yet providing higher electric fields without damages. Moreover, we analyze electro-mechanical properties of CGO thin films grown on perovskite such as $SrTiO_3$ (STO). Microstructure and electrostriction analysis indicate a perfect microstructure without grain boundaries barriers or defects.

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Keywords: CGO, Electrostriction, Lead-free

ABS 873

ENHANCING DIELECTRIC PROPERTIES OF BARIUM TITANATE MACROFIBERS

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Piezoelectric fibers are widely used in composites for actuator and sensor applications due to its ability to convert electrical pulses into mechanical vibrations and transform the returned mechanical vibrations back into electrical signal. They are beneficial for the fabrication of composites especially 1-3 composites, active fiber composites (unidirectional axially aligned piezoelectric fibers sandwiched between interdigitated electrodes and embedded in a polymer matrix) etc., with potential applications in medical imaging, structural health monitoring, en-ergy harvesting, vibration and noise control. For several decades, lead zirconate titanate (PZT) fibers have been the major active component in these composites. Although, fibers made of PZT based systems are commercially available in the market, their piezoelectric behavior is seldom analyzed due to the complexity in measurement. In the past decade, the interest in pie-zoelectric composites is shifted to active components with lead-free piezoelectric fibers. Alt-hough, literature on such lead-free piezoelectric fibers are found, their piezoelectric properties are rarely reported.

In this contribution, piezoelectric BaTiO3 fibers fabricated using thermoplastic extru-sion and their electromechanical properties are investigated. Additionally, nanofibers of BaTiO3 are manufactured using electrospinning and their influence on the extruded BaTiO3 fi-bers is studied. The nanofibers are incorporated in the BaTiO3 feedstock and extruded as a macrofiber and sintered. Such fibers show a substantial increase in polarization and strain compared to the BaTiO3 fibers without any nanofibers.

Keywords: ferroelectric, barium titanate, piezoelectric fibers

ABS 872

NEW TECHNIQUE FOR DEAD LAYER ANALYSIS IN THIN FILM FERROELECTRIC CERAMICS

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Conception of a passive dead layer at the metal-ferroelectric interface plays an important role in electrical properties characterization of ferroelectric thin film ceramics. This layer is considered as a reason for properties degradation with the ferroelectric ceramics film thickness decrease, including decreasing polarization, hysteresis slope, dielectric permittivity, etc. Origin of the dead layer may be associated with physical or technological issues however it is an important limiting factor for example in FRAM scaling. In the present work we consider different techniques for experimental estimation of the dead layer value in different lead zirconate-titanate (PZT) films.

We propose a new dead layer estimation technique based on the dielectric portraits analysis (the polarization dependence of the hysteresis loop tips on the voltage). A comparative analysis with Tagantsev's [1] and small-signal capacitance techniques is performed.

The dead layer model is used for the analysis of dense and porous thin films. The dead layer thickness ld was calculated from the dielectric portrait slopes that exclude leakage influence. For comparison, the dead layer thickness was obtained from the dielectric permittivity versus thickness dependence obtained from high frequency small-signal measurements, and from slopes of the hysteresis loops at the coercive field point. The small-signal capacitance technique and the method based on the dielectric hysteresis portraits give good correlation for dense PZT films: ld ~ 2.13-2.2 Å. For porous PZT films the dead layer thickness demonstrates higher values: ld = 12 Å for capacitance small-signal measurements, and only ld = 5.8 Å for measurements based on the dielectric portrait. This suggests that higher leakage conductivity shunts the electric capacitance of the dead layer with a higher thickness and a lower dielectric constant, and therefore reduces its effective thickness. Tagantsev's technique gives twice-triple lower ld values due to effect of nonlinear leakage currents and relaxation losses.

Thus the proposed techniques make it possible to perform a correct dead layer analysis in thin film ferroelectric ceramics.

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Keywords: ferroelectric thin films, PZT ceramics, dead layer

ABS 870

THE STRUCTURAL AND DIELECTRIC PROPERTIES OF ANT CERAMICS

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Ag(Nb1-xTaX)O3 (x = 0–0.8) ceramics were prepared using asolid-state reaction method, and the microstructure, dielectric abnormalities, polar order and microwave dielectric properties were characterized. A single phase was identified using XRD for dense ceramics with x = 0–0.65, while small Ag precipitates and microstructural inhomogeneities were observed with BSE-SEM and EDS. A higher sintering temperature helps to improve the homogenous distribution of the Nb and Ta, while it may also result in the decomposition of the Ag(Nb1-xTaX)O3 perovskite phase. Four kinds of dielectric abnormalities at RF frequencies were observed in the temperature range -150 to 300°C. Only the peak in the dielectric constant can be observed for P1, which is due to the M2–M3 phase transition. Both the peaks in the dielectric constant and the dielectric loss are observable for P2 and P3, while they do not correspondto any structural phase transition. As a new dielectric abnormality that has not been paid attention to before, P4 exhibits a strong relaxation in the dielectric loss, while no abnormality in the dielectric constant can be observed. The dielectric relaxation for P4 fits well to an Arrhenius equation, indicating a thermally activated process that is probably related with the Ag precipitates. The dielectric tunability measurement at 20–80°C reveals ferrielectricity for for x = 0–0.2, antiferroelectricity for x = 0.5, and a transition behaviour for x = 0.35. Combining these results with the phase diagram, it can be concluded that the ferrielectric–antiferroelectric transition does not correspond to the M1–M2 phase transition. The microwave dielectric constant for the Ag(Nb1-xTaX)O3 ceramics reaches its maximum value at x = 0.35, while the Qf value and the temperature coefficient of resonant frequency increase monotonously with the value of x. Further work should be carried out to further clarifythe origin of the P2, P3 and P4 dielectric abnormalities, the relationship between microstructure and dielectric properties, and the ferrielectric–antiferroelectric transition.

Keywords: ANT, Microwave ceramics, Phase transitions

ABS 927

SOL-GEL SYNTHESIS AND HUMIDITY SENSING FEATURES OF IRON-DOPED SYNTHETIC SEPIOLITE

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Synthesis of clay minerals gives the possibilities to obtain new materials with better performances towards a specific application. However, few papers deal with the synthesis of sepiolite-like. Therefore, a new iron-doped magnesium silicate nano-powder was prepared by a simple sol gel route and its humidity sensing properties were evaluated.

For this aim: Tetraethyl orthosilicate was mixed with ethanol (EtOH), in the meantime, a solution of Mg(NO3)2.6H2O was prepared in a distilled water then, added dropwise to the former solution and refluxed until the formation of gel (noted as S1). The obtained gel was dried in an oven at 120°C overnight, prior to calcination at 500°C for 5 h to eliminate all by-products. Then, in a second sample (S10) 10% Mg2+ ions were replaced by Fe3+ ones by adding Fe(NO3)3.9H2O after that, the formed gel was washed thoroughly. Finally, 2 g of the washed sample were added to NH4OH solution and put at 80°C in a sealed container for about 48 h to peptize the washed gel (i.e. to transform it into a sol). After that, the prepared sol was dried in an oven and heat treated at 500°C for 2 h. A screen-printing ink was obtained by dissolving completely Fe(NO3)3.9H2O in EtOH, under magnetic stirring, followed by the addition of mono-ethanol amine + terpenol under continuous stirring. Then, S1 and S10 were added progressively to this solution. The obtained inks were screen-printed onto an alumina substrate with interdigitated Pt electrodes and dried overnight at room temperature. Finally, the films were fired at 550°C for 1 h. The sensors were tested at 25°C in a laboratory apparatus in which relative humidity could be varied between 0 and 96% by steps, each one of 3 min. The sensors resistance was determined by LCR meter.

Particle size distribution showed that the S10 heat-treated at 500°C has a lower average diameter with respect to S1 (18.5 and 88.5 micron, respectively). In the peptized dried sol, grains in the agglomerates were below 100 nm as observed by SEM. XRD patterns of fired S1 and S10 were amorphous. IR spectra showed that the samples exhibited characteristic vibrations of magnesium silicates, whatever the presence of iron atoms or not. The X-ray spectroscopy peaks for Fe3p and Fe 2p3/2 showed an energy shift to higher binding energy of 1.1 and 0.5 eV, indicating that iron silicides phases were formed [1, 2].

Findings show that an iron-doped magnesium silicate nano-powder was successfully synthesized by a sol gel process with a simple and low-cost method once screen-printed, sensors were highly sensitive to humidity from 40 RH%. S10 showed a slight response to water vapor from about 18 RH%, probably due to the presence of iron oxide. Response and recovery times were in the order of some minutes.

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Keywords: Electroceramics, sepiolite, humidity sensor

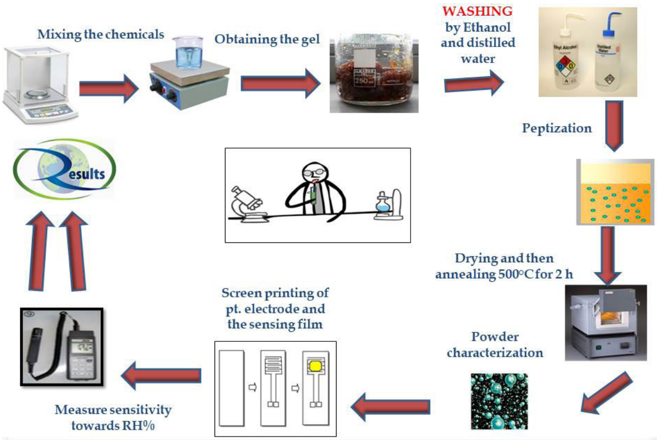

Fig. 1 Schematic of the synthesis of synthetic sepiolite and sensors

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M-AND W-TYPE HEXAGONAL FERRITES AS PERMANENT MAGNETS OR MICROWAVE MATERIALS

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Hexagonal ferrites represent a family of technically important magnetic materials. We investigated three hexagonal ferrites from the Fe-rich part of the pseudo-binary system SrO-Fe2O3. Besides the well-known M-type SrFe12O19 two other ferrites were found to exist at high temperatures: W-type SrFe2Fe16O27 and X-type Sr2Fe2Fe28O46 ferrites. A detailed characterization of the X-type Sr-ferrite is reported here for the first time using XRD, HRTEM, magnetization measurements, Mössbauer and 57Fe NMR spectroscopies. The results are compared to those of W- and M-type Sr ferrites. Mössbauer spectra were analyzed with six Fe contributions in the case of the X-type, seven Fe-sites for the W-type and five Fe sites for the M-type in agreement with crystal structure arrangements. Based on a detailed analysis of the NMR spectra the NMR lines were assigned to individual crystal sites. A preferential occupation of ferrous ions in the S blocks of the X- and W-type ferrites was elucidated from Mössbauer and NMR data.

Besides M-type ferrite, W-type ferrite was proposed as alternative permanent magnetic material. However, this material has limited stability in air at high temperatures only. We have performed a detailed study on the phase stability limits of W-type SrFe18O27 as function of T and pO2. We also report on the nonstoichiometry and magnetic properties of this ferrite at 1300°C at different pO2. Alternatively, Zn-substituted W-type ferrite is stable in air and exhibits a large magnetization, which qualifies this ferrite as a promising hard magnetic material.

Sc-substituted M-type SrScxFe12-xO19 ferrite has attracted interest as nonreciprocal microwave ferrite. Single-phase samples were obtained for 0 <= x <= 2, and their coercivity, anisotropy field and ferromagnetic resonance frequency decrease with x. We show, that this ferrite is a promising candidate material for nonlinear components (e.g. circulators) operating at Ka band frequencies. Bulk samples as well as thick films with textured microstructure are integrated as self-biasing microwave magnetic components into LTCC multilayer modules for satellite communication systems.

Keywords: Hexagonal ferrites, phase stability, microwave ferrites

ABS 866

$\mathrm{GaV_4S_8}$ AND $\mathrm{GaV_4Se_8}$ POWDERS AND CERAMICS FOR THE INVESTIGATION OF MULTIFERROIC SKYRMIONS

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Skyrmions are vortex filaments of vector fields, similar to Abrikosov vortexes in superconductors. Recently, theoretically predicted magnetic skyrmions were experimentally discovered in the several chiral ferromagnets. The diameter of these chiral magnetization whirls (fig. 1a) is of the order of hundred nanometers so these materials promise applications as extremely high density memory storage media. GaV4S8 and GaV4Se8 are even more intriguing skyrmion hosts as there the magnetic filament is decorated by a filament of electric polarization. Investigation of functional properties of these multiferroic skyrmions requires to prepare GaV4S8 and GaV4Se8 materials in the form of epitaxial films. Fabrication of good quality ceramic targets can chiefly contribute to this aim.

GaV4S8 and GaV4Se8 were synthesized by direct single-step synthesis from elements. Sulfur (or selenium) and vanadium powders were mixed with lumps of gallium. The mixture was heated slightly by infrared lamp to melt gallium and ground and mixed in an agate mortar. The reaction mixture was put into the silica glass ampoule previously filled by argon. The ampoule was evacuated by a rotary pump, filled by argon, again evacuated, filled by argon, finally evacuated to residual argon pressure of about 2 mbar and sealed. The ampoule with reaction mixture was slowly heated by a rate of 40 K/h to 990 °C in a chamber furnace, annealed for 7 days and cooled at 10 K/min. The slow heating is necessary to allow the reaction of sulfur, at quick heating the high pressure of sulfur can burst the ampoule. Unlike other this single-step synthesis resulted in pure single-phase GaV4S8 and GaV4Se8 powders as was proved by X-ray diffraction.

GaV4Se8 was prepared only in the form of fine-crystalline powders, GaV4S8 was prepared in the form of ceramics additionally. The powder was pressed by a uniaxial press in dies of diameters 13 mm and 20 mm respectively, at a pressure of 380 MPa. The sintering was done again in a sealed silica glass ampoule by the same annealing procedure as for the synthesis of powders. The resulting ceramic GaV4S8 target (fig. 1b) has 99% purity according to XRD, it contains about 1% of unidentified impurity. The target will serve for pulsed laser deposition of thin films or for microwave sputtering. This work has been supported by the Czech Science Foundation (project no. 17-11494J).

Keywords: skyrmions, multiferroics, solid-state synthesis

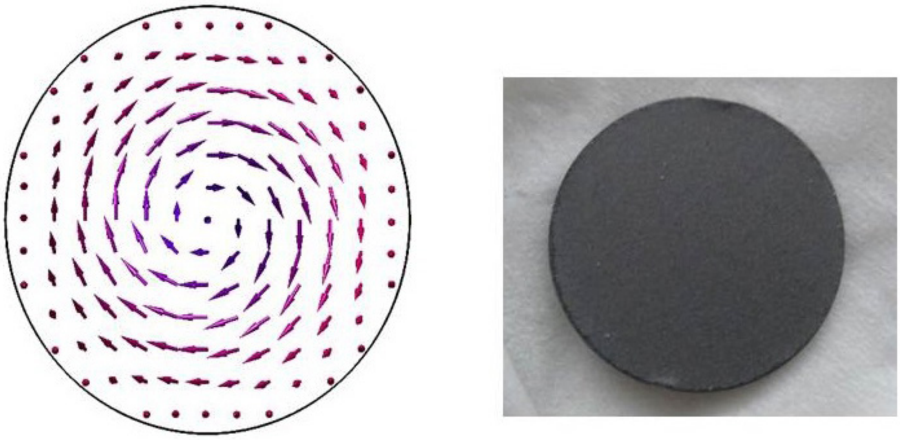

Fig.1

a) The cut through skyrmion filament - general scheme

b) $\mathrm{GaV_4S_8}$ ceramic target (20 mm in diameter)

ABS 865

THE EFFECTS OF BISMUTH OXIDE DOPING ON ELECTRICAL PROPERTIES OF MAGNESIUM FERRITE SINTERED BODIES

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In this research, dielectric properties of bismuth doped Mg-ferrite were evaluated and series of samples, $[MgO.(Fe2O3)1-x(Bi2O3)x$, x=0, 0.01, 0.02, 0.04, 0.08], were prepared. Bismuth oxide doped Mg-ferrite powders were prepared by the solid state reaction of oxides at 900 °C. Prepared powders were granulated, pressed cold isostatically into pellets and sintered at 1150 °C for 4 hours. Magnetization saturations of the samples were decreased upon bismuth doping from 20 to 14 emu/g. Dielectric constant and dielectric loss were decreased by bismuth doping, as shown in Figure 1(a-c). The measured values for dielectric constant and dielectric loss are 32 and 0.12 for 0.08 mol% bismuth doped sample at 1 MHz, respectively which the dielectric constant is higher than reported values in the literature and dielectric loss is the same level of the reported values. Bismuth ions are responsible for increasing the dielectric constant due to their high polarizability contributed to the lattice of magnesium ferrite. Moreover, by increasing the level of bismuth doping, a secondary phase with high electrical resistance forms in the grain boundary which is responsible for such a low dielectric loss. Varistor properties further confirmed existence of the bismuth oxide rich high resistance phase as intergranular layer. Figure 2(a) shows I-V characteristic curves of samples with different amounts of bismuth oxide. Samples with 0.01, 0.02 and 0.04 mol% exhibit varistor properties where a samples with 0 and 0.08 mol% show ohmic behavior. Figure 2(b) shows the EDS layered of bismuth doped Mg-ferrite. The secondary phase was also detected by scanning electron microscopy observations. In conclusion, low loss samples with high dielectric constant were prepared by bismuth doping of magnesium ferrite.

Keywords: Magnesium Ferrite, dielectric constant, dielectric loss

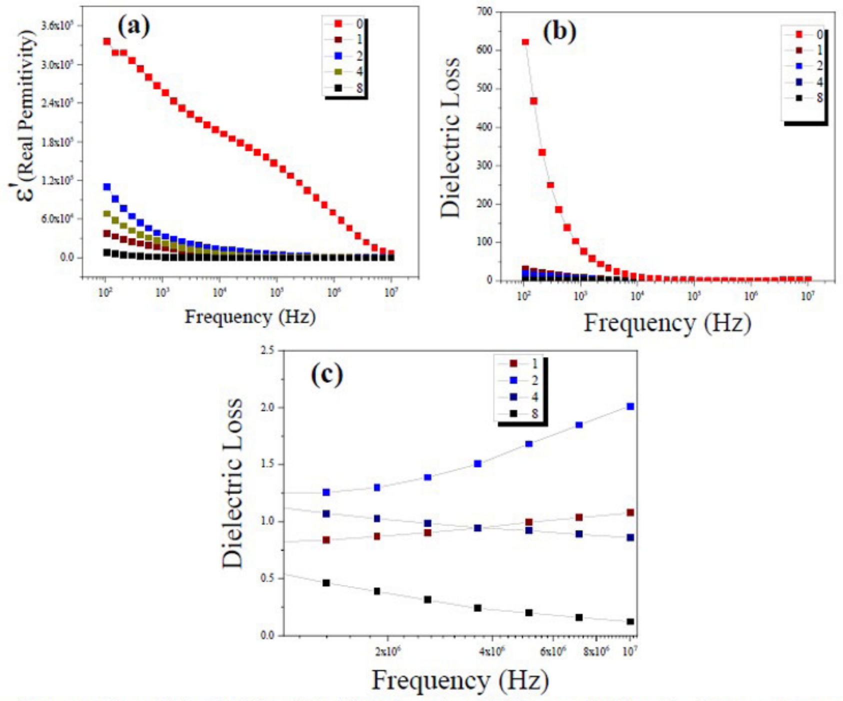

Figure 1. Real permittivity (a), dielectric loss (b-c) of samples with different mol % bismuth oxide versus frequency

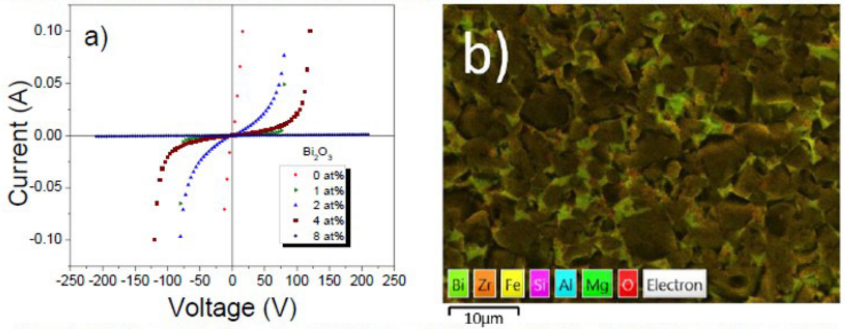

Figure 2. I-V characteristic of samples with different mol% bismuth oxide (a) and (b) EDS layered image of 0.04 mol% bismuth doped Mg-ferrite.

ABS 864

INTERPHASE AND DOMAIN WALL MOTION IN FERROELECTRIC FILMS AS PROBED BY IN-SITU X-RAY DIFFRACTION DURING ELECTRICAL BIASING

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Piezoelectric and ferroelectric thin films are ubiquitous in many applications such as sensors, actuators, pyroelectric devices or advanced memories. The case of polycrystalline thin films is particularly complex and delicate to model. Several effects (i.e. interface, substrate clamping, grain boundary, stress) affect the behavior of the domains at the local scale and by consequence impose the film macroscopic response.
It will be shown in this communication how in-situ X-ray diffraction during electrical biasing (DC or AC mode) offers unique information to address these complex behaviors at different scales. The case of the prototypal Pb (Zr48, Ti52) O3 or PZT films will be discussed. These films at the morphotropic phase boundary (MPB) are composed of two textured ferroelectric phases (one tetragonal and the other rhombohedral). It has been observed that interphase boundary motion is the predominant effect during the biasing. A strong heterogeneity from grain to grain and as a function of the depth in the film has also been observed [1].
Our results are based a combination of synchrotron beamtimes as well as results from our in-situ lab source based setup [2]. Finally, the ability to image ferroelastic domains by coherent diffraction techniques (or CBDI) will be discussed.

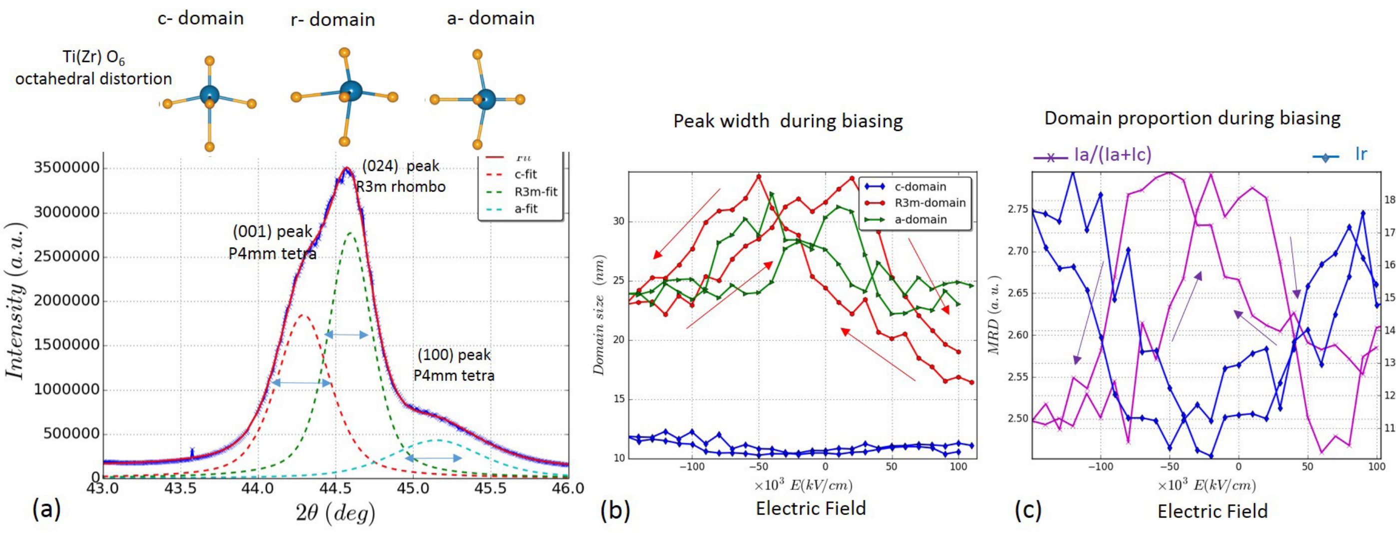
Reference

[1] Vaxelaire et al Jour.of Appl. Phys. 120, 104101(2016)
[2] Allouche et al, Materials & Design 154, 340 (2018)

Caption

Figure 1: A diffraction peak (1) is recorded for each bias where the contribution of three domain variants is quantified. The FWHM (related in first approximation to the domain size) (2) and the intensity of the 3 variants (3) (related to domain fraction) present a typical butterfly shape as a function of the electrical field.

Keywords: In-situ XRD, Domain, Morphotropic phase boundary



ABS 80

SINTERING OF HOLMIUM-DOPED LUTETIUM OXIDE BY SPARK PLASMA SINTERING FOR HIGH POWER LASERS AMPLIFICATION IN Mid-IR

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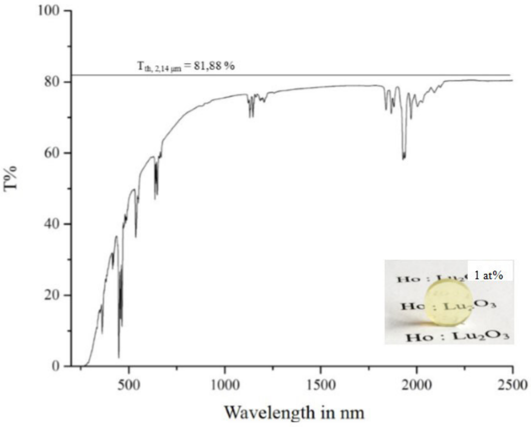
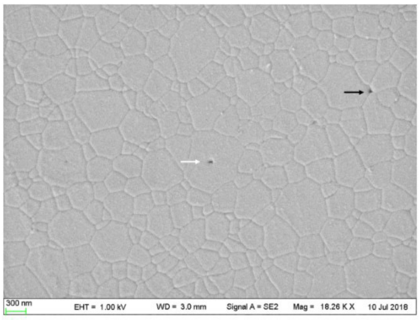
Aim of MISTRAL project (Mid-IR Terawatt Laser) is to develop new transparent ceramics for high power lasers emitting at 2.1 µm by doping with Ho3+. The particularity of this wavelength is its strong absorption by water, which makes those lasers very attractive for medical applications. This material is very promising to be used as laser medium thanks to its high thermal conductivity and low phonon energy. Moreover, ceramic route is less expensive, easier and faster to perform than crystalline growth.
During this project, the manufacturing of full-dense Ho3+:Lu2O3 has been investigated by implementing an integrated approach of the ceramic process (i.e. from the synthesis of the specific powders to the sintering step). So, the synthesis of nanosized lutetium oxide-based particles was firstly studied. Commercial oxides were dissolved in nitric acid and then co-precipitated to obtain highly pure and nanometric powder. After calcination in air, Ho:Lu2O3 powder with an average size of 50 nm was obtained. Green compacts are obtained by slip-casting or by dry pressing and are sintered by SPS at 1400 °C. Sintering of Ho-doped lutetium oxide by Spark Plasma Sintering, which has a higher thermal conductivity than YAG, will be performed to obtain fully dense material.





A maximum of transmittance at 80 %, which was close to the theoretical transmittance at 2.14 µm, was obtained for doping of 1 and 10 at.%Ho. Absorption bands are in agreement with absorption of Ho3+ ion in the Lu3+ site in cubic structure of Lu2O3 (Fig). A decrease of transmittance from 1000 nm to 200 nm indicates the presence of residual porosity remaining after SPS. This residual porosity, visible on microstructures, can be intra (white arrow) or intergranular (black arrow).
In order to eliminate it, an optimization of sintering step is necessary. For that, influence of Ho3+ concentration has been studied on densification rate and on final microstructure (i.e. grain size and grain boundary segregation). Sample with higher density and transparency are obtain with a higher concentration of Ho3+ (10 at.%) showing a benefic effect of dopant on final microstructure and a facilitation of sintering step.
Fully dense transparent Ho:Lu2O3 ceramics have been successfully sintered by SPS with different doping (1-10 at.%Ho). Transmittances of all samples are close to 80 % in 1.5-2.5 µm range. A sintering study by plotting sintering trajectories with different holmium concentrations will be carried out in order to determine its influence on densification and grains growth mechanisms.

Keywords: Rare-earth Sesquioxides, Mid-IR, Sintering

ABS 69

MECHANICAL PROPERTIES, WEAR RESISTANCE AND SURFACE DAMAGE OF GLASSES AND $MgAl_2O_4$ SPINEL CERAMIC AFTER ABRASION AND SCRATCH EXPOSURE

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A transparent spinel ceramic is compared to different types of glasses as well as a polymer in terms of mechanical behavior and optical appearance before and after mechanical exposure. The mechanical behavior of the materials are compared on the basis of depth-sensitive indentation and ring-on-ring bending tests, deriving representative load dependent hardness, elastic modulus and fracture stress values. As main focus, the specimens have been analyzed after certain exposure times of sand blasting and different loads during scratch tests via weight balance, confocal laser scanning and optical microscopes to assess wear resistance in terms of surface roughness, mass loss, critical loads and initial damage.

The ceramic called Perlucor® is available at CeramTec Etec with the classical stoichiometry MgAl2O4. In this comparative study common transparent materials like a Polycarbonate as well as different hardened and unhardened glasses like float glass or Borofloat® by Schott, especially Gorilla glass® by Corning, are studied. Young´s modulus E was measured by an impulse excitation technique, hardness H with depth sensitive micro-indentations and fracture toughness KIc was calculated from the crack lengths using the equation by Anstis et al. Ring-on-ring bending experiments were executed in an electromechanical testing machine. The experimental data were used in a statistical analysis to derive in addition to the average fracture stress also the characteristic strength and Weibull modulus by linear regression.

For the sandblasting a special sample holder was designed, see Figure 1. After certain exposure times the samples were optically investigated with a reflex camera. The mass loss and surface roughness was calculated. Three scratches on each sample were carried out with a sphero-conical diamond tip under a load increasing from 0.03 N up to 5 N and optical analyzed.

Table 1: Used materials and their properties, E, H and K_{IC} derived in the current work. ρ and ν from [21-27]

Material	ρ [g cm^{-3}]	ν	E [GPa]	H [GPa]	K_{Ic} [MPa√m]
Perlucor	3.57	0.25	287 ± 6.5	18.5 ± 0.4	2.51 ± 0.6
Polycarbonate	1.2	0.4	7.3 ± 2.4	0.2 ± 0.1	-
NBK-7	2.51	0.206	90.2 ± 0.9	8.1 ± 0.07	0.52 ± 0.04
Float glass	2.5	0.2	75.6 ± 1.4	7.2 ± 0.04	0.59 ± 0.06
Float glass hardened	2.5	0.2	72.6 ± 1.7	8.1 ± 0.14	2.07 ± 0.07
Borofloat	2.2	0.2	78.0 ± 0.2	7.2 ± 0.02	1.15 ± 0.13
Borofloat hardened	2.2	0.2	78.4 ± 0.1	7.8 ± 0.02	2.53 ± 0.25
Gorilla glass	2.43	0.21	71.2 ± 0.5	7.1 ± 0.07	0.91 ± 0.03
Gorilla glass hardened	2.43	0.21	67.2 ± 0.2	8.4 ± 0.02	3.02 ± 0.12
B270	2.55	0.219	75.8 ± 0.3	7.3 ± 0.03	0.64 ± 0.06
B270 hardened	2.55	0.219	80.6 ± 0.5	7.7 ± 0.06	1.89 ± 0.12

Comparisson and ranking.

Perlucor showed by far the highest hardness and withstood the sandblasting and scratch exposure very well. Hardened Gorilla glass has the highest fracture strength and fracture toughness as well as a very high value for the hardness, but seems to be prone to scratching and gets faster blurred than the ceramic. Hardened B270 displayed the best scratch values of the hardened glasses and also quite high hardness and fracture strength, while performing was bad during the sandblasting exposure with the biggest mass loss. N-BK7 can be considered as an average glass, all in all every unhardened glass behaved analogically with properties very close to each other.

Keywords: Transparent Spinell Ceramic, Wear resistance, mechanical properties

ABS 68

EVALUATION OF THE RESIDUAL POROSITY OF TRANSPARENT MATERIALS

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Microstructure analysis is an urgent issue in modern materials science. Functional properties of laser materials (single crystals, glasses, ceramics) are mostly governed by their microstructure, particularly, by the residual porosity. For example, laser efficiency of ceramic samples are the same as for commercial single crystals and glasses if residual pore concentration is below 10-4 vol%. At the same time, the ways to visualize such low residual porosity and to evaluate it carefully are still being developed. Present work attempts to develop a method for evaluating pore size distribution in transparent material's bulk using experimental measurements of pore sizes determined from the cross-section.

As model systems, 1-4 at% Nd3+:YAG transparent ceramics were used to validate presented method by comparing its results with other known approaches. Ceramic samples were produced by reactive sintering using high purity commercial oxides and SiO2 aid (0.14 wt%). Porosity of ceramics was studied using confocal laser scanning microscopy on a device LSM 800 (ZEISS, Germany). To visualize bulk porosity, regions ("slices") were merged using microscope software into 3D images. To calculate pore size from the cross-section and their quantity, slices in the region were merged along z axis and were represented in the xy plane. At finish, residual porosity was calculated for each ceramic sample according proposed original mathematical model.

3D models of pore size distributions in the bulk of 1-4 at% Nd3+:YAG have been built. Mean pore section sizes Deq. obtained from LSM range in 160-190 nm for 1-3 at% Nd3+:YAG ceramics and increase to 286 nm for 4 at% sample. Increasing activator ions content has been shown to reduce ceramics quality, particularly, for samples with c(Nd3+)>2 at% the non-uniform pore distribution and pore aggregation are observed. This is due to amount of SiO2 was not optimized, which role is to reduce mechanical strains in Nd3+:YAG solid solutions. 1-4 at% Nd3+:YAG ceramics possess in-line optical transmittance coefficient of 82-80% at the wavelength λ=1064 nm and residual porosity ranging from 0.0009 to 0.0112 vol%.

Suggested method enables one to evaluate residual porosity correctly.

Acknowledgements
This work was financially supported by the Russian Science Foundation (Project No. 18-73-00145).

Keywords: Residual porosity, Transparent ceramics, Optical properties

ABS 862

TEXTURED PIEZOELECTRIC CuO-DOPED PIN-PMN-PT CERAMICS

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Ternary lead-based Pb(In1/2Nb1/2)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PIN-PMN-PT) ferroelectric ceramics are leading candidates for next-generation textured piezoelectrics. Fabrication of textured ceramics requires high sintering temperatures of ~1200°C-1250°C which results in volatility of certain constituents (e.g. PbO). We mitigate the problem by lowering the sintering temperature through a combination of reactive sintering and CuO-doping. In situ XRD studies of perovskite phase formation during reactive sintering show that CuO reduces the temperature required for perovskite formation by ~25°C and reduces second phase pyrochlore formation. The combination of reactive sintering and 0.5 mol% CuO doping reduces the sintering temperature to 790°C or ~240°C lower than conventional sintering. The addition of 0.5 mole% CuO dopant also reduces the activation energy for reactive sintering from 690 kJ/mol to 328 kJ/mol. In this work, textured CuO-doped PIN-PMN-PT ceramics were also fabricated at lower processing temperatures by reactive templated grain growth (RTGG). BaTiO3 microcrystal platelets were chosen to seed the phase transformation of the PIN-PMN-PT perovskite and impart [001]C crystallographic orientation of the textured PIN-PMN-PT ceramics.

Keywords: Textured, Piezoelectric, Ceramics

ABS 861

FABRICATION OF TRANSPARENT CERAMIC OPTICAL COMPONENTS (MICRO LENSES, MICRO PRISMS, FRESNEL ZONE PLATES) VIA LOW PRESSURE INJECTION MOLDING

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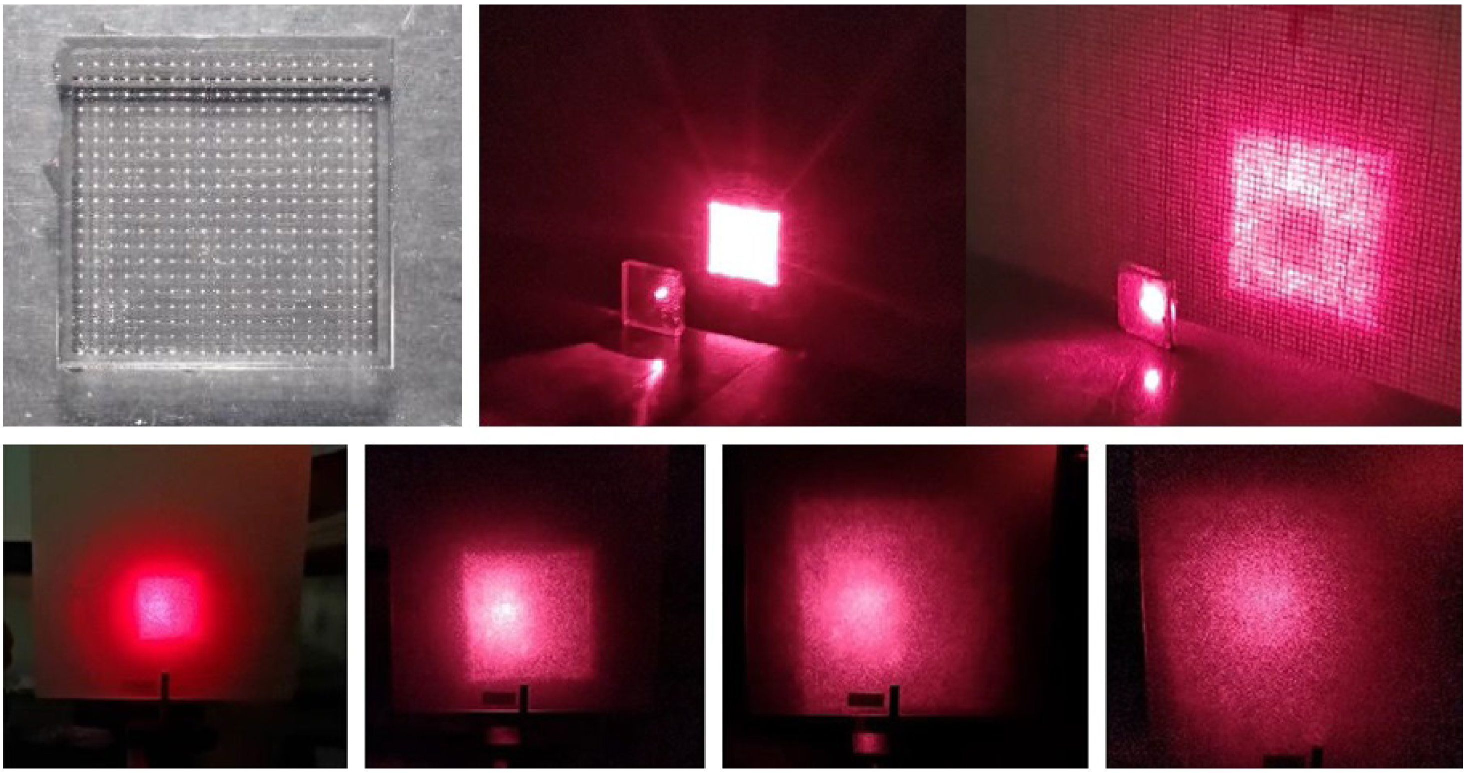
Based on cubic zirconium oxide (Tosoh), ceramic compositions for low-pressure injection moulding were developed using a specially developed step-by-step preparation process in order to produce and characterise near-net-shape transparent microlens arrays, microprisms and Fresnel zone plates. The rheological properties of the casting compounds were characterized and optimized for the subsequent forming process. Furthermore, a suitable thermal process consisting of debinding, sintering and hot isostatic post-compaction was developed. Subsequently, the microstructural and surface properties as well as the optical imaging properties of the components were investigated. The individual development steps and their results are presented.

Keywords: transparent optical ceramics, micro lense, prism, zone plate, low pressure injection molding



ABS 33

THE PROCESSING OF PURE KNN CERAMICS: TWO-STEP SINTERING VS CONVENTIONAL ONE-STEP SINTERING

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The two-step sintering method has been successfully applied to fabricate lead-free alkaline niobate (K0.5Na0.5NbO3 - KNN) piezoelectric ceramics. Investigation of the sintering behaviour of these ceramics in terms of sinterability, microstructural evolution and piezoelectric properties demonstrated that the two-step sintering (TSS) method can not only decrease sintering temperature effectively, but also enhance densification. The higher density and lower K and Na elemental loss that was achieved via the use of two-step sintering yielded improved piezoelectric properties compared to samples made using conventional one-step sintering.

Na2CO3, K2CO3 and Nb2O5 were used as raw materials and calcined at 900°C for 2 h. The resulting (K0.5Na0.5)NbO3 powders were mixed with 1 wt% PVA and pressed into pellets using 200 MPa. Densification was achieved using both single step sintering and two-step sintering. For the former the dwell temperature and time were in the range of 1080 – 1140oC for 2 h and a heating rate of 5oC/min was used; the sample was allowed to cool naturally. With two-step sintering, the first step involved heating up the samples to an initial temperature, T1, in the range 1040 – 1140oC using a heating rate of 10oC/min and very short soak of 10 mins. Then the samples were cooled rapidly down, at 30oC/min, to a lower temperature, T2, in the range 1030 – 1070oC and soaked for 10 – 20 hours.

Compared to the single step approach, the two-step sintered KNN ceramics demonstrated a slightly improved density of 94.5% of theoretical density compared to 91%. When the optimum 2-step conditions were used, these were T1 = 1120°C for 10 min and T2 = 1070oC for 10 h, the samples exhibited excellent piezoelectric and dielectric characteristics; the piezoelectric charge coefficient, relative permittivity, dielectric loss and mechanical quality factor were 117 pC/N, 337.6, 6.41% and 51.9, respectively. These compare favourably with the typical values of 112 pC/N, 298.6, 11.09% and 32.3, respectively, for conventionally sintered KNN ceramics of the same composition.

The results suggest that two-step sintering could be an effective approach to solving the problem of poor sinterability of ceramics and hence allow the fabrication of high-performance KNN-based ceramics.

Keywords: Potassium sodium niobate, Piezoceramic, Two-step sintering

ABS 8

IMPROVEMENT IN ELECTRICAL DEGRADATION AND STABILITY OF ZINC OXIDE VARISTORS WITH BORON OXIDE ADDITIVES

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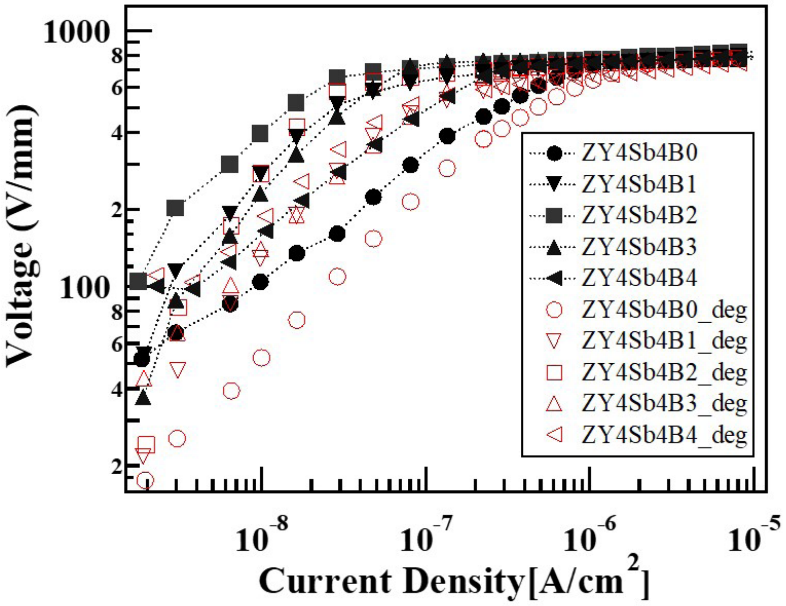
ZnO-based varistors are widely used in different circuits and power systems as surge absorbers. The typical high nonlinear voltage –current (V- I) characteristics of ZnO varistors make them effective devices to protect against high voltage surge and electrostatic discharge. Double Schottky barriers formed between ZnO grains is a main feature of a varistor. By doping several kinds of additives, the I-V characteristics change remarkably. However, the electrical degradation occurs under continued voltage simultaneously. The microstructural and electrical characteristics of Zn-Bi-Mn-Co-Cr-Ni-Y-Sb varistor ceramics doped with B2O3 have been investigated in order to increase both the varistor voltage and the resistance of electrical degradation by changing the amount and the molar ration of Y and Sb. However, it was not satisfactory although the resistance of degradation could be improved. It is speculated that the electrical degradation is caused by the motion of Zn2+ and oxide ions (O2-) under the voltage application. Thus, in this study, addition of B2O3 was examined to block the motion of these mobile species. ZnO varistors were fabricated from ZnO, Bi2O3, MnO2, Co3O4, Cr2O3, and NiO powders as basic additives and Sb2O3, Y2O3, SiO2, B2O3 powders. A pressed tablet of the mixture was then calcined at 600°C for 5 h in air, sintered at 1150°C for 3 h in air, and then allowed to cool to room temperature. Aluminum electrodes were formed on both faces of each sample to measure the V–I characteristics and isothermal Capacitance transient spectroscopy (ICTS) signal. The crystal structure (XRD) and the chemical composition (EDS), and the surface state (SEM, BSE) were evaluated. It is found from element mapping by EDS that The Sb atoms shifted to Bi-Y-O phase along the grain boundaries of ZnO grains by adding the proper amount of B2O. Mean grain size did not change much with increasing amount of B2O3. For samples with SiO2, it was found from XRD analysis that the Bi2O3 diffraction peaks intensity decreased or disappeared by increasing the amount of B2O3. The varistor voltage of the ceramics was stable around a high voltage from 900 to 1100 V/mm. It is confirmed by the leakage current-time characteristics measure at 130°C that the resistance to electrical degradation of samples was improved drastically by adding B2O3 of 1mol%. It was conjectured that excess Sb atoms enhance the motion of mobile species.

Keywords: ZnO varistor, boron oxide doped, electrical degradation



S08

SILICATE CERAMICS

INVITED LECTURES

ABS 793

SUSTAINABILITY OF CERAMIC PROCESS: ENVIRONMENTAL IMPACT AND SILIFE PROJECT

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This work deals with the relationships between ceramics and the environment, considering Ceramic District in Sassuolo, where is concentrated the 85% of Italian production of tiles, as a case of study. The Italian ceramic tile industry has a long and significant experience in prevention and reduction of environmental impacts, due to the high concentration of factories and the climatic profiles of that territory. The specific experience of the Italian ceramic tile sector is used to concretely quantify and assess the environmental results achieved, as well as to show and discuss an approach that may be applied to other sectors. This publication shows the most significant environmental impacts, duly quantified by means of different appropriate parameters, applicable to the ceramic tile manufacture: emission into the atmosphere, water footprint, energy consumption, greenhouse gas. The quite good environmental performances achieved by ceramic tiles are worthy of exploitation in marketing and product policies, taking into account that now the protection of the environment as a whole and sustainable development are more and more considered fundamental objectives by an increasing number of people worldwide and users of ceramic materials as well. First policies and management systems regarding environment like ISO 14001 and EMAS has been developed, but new assessment and communication tools (environmental labels) have been made available for product environmental quality: Type I (environmentally excellent products), Type III (EPD), Ecolabel. More and more nowadays the sustainability is the driver for the competitiveness of ceramics in the global market. This interest has also been found within the ISO Technical Committee TC 189 'ceramic tiles', where a new standard containing specifications for sustainable ceramic tiles has been completed for approval. In this document among all the parameters to be evaluated strictly related to environmental issue, there are also economic and social criteria, such as for example the health and safety of the workplace. In particular one of the professional disease which could affect the ceramic industry is the RCS. Due to the fact that quartz can't be replaced, what can be done is to reduce the toxicity of the substance with some treatment. Currently SILIFE project is in progress with the aim to produce commercial coated quartz powder, that shows reduced toxicity. All the stakeholders has been involved: the industries and their association, authorities and the university research showing how an integrated system among producers, territory and research could reach excellent performances.

Keywords: sustainability of tiles, respirable crystalline silica, silife project

ABS 778

LATEST PROCESS INNOVATIONS IN CERAMIC TILES MANUFACTURING

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Ceramic tile production is nowadays moving to ever larger tiles or big slabs, with the aim to fulfil the increasing demand of new products for building and constructions.
As a matter of fact the reliability of both forming and firing technologies allowed a continuous increase of tile sizes, thus achieving higher added value products.

Moreover the huge development of digital decoration technologies has undoubtedly revolutionized the production process of ceramic tiles, mainly by increasing the graphic quality of finished products but even by giving many opportunities to optimize the lay-out and the running operations of the glazing.

Actually the potentialities of ink-jet technologies applied in the ceramic decoration process are universally recognized, resulting in a much easier design of new products joined with high constancy and yields of the production quality.

The present article aims at highlighting the most recent innovations in ceramic tiles manufacturing achieved through the introduction of new technologies, which afford better product qualities and fully controlled processes.

The main technical features of the production process (forming, decorating, firing and finishing) have been examined by analyzing the technological parameters of intermediate and finished ceramic products.

Finally, as a result of the latest developments, traditional ceramic productions are really turning to highly automated industries by taking great advantage of the 4.0 revolution.

Keywords: Tiles, Ceramic slabs, Manufacturing process

ABS 611

ONE-PART ALKALI-ACTIVATED MATERIALS WITH HIGH SULFURIC ACID RESISTANCE

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Objective Materials with a high acid resistance are required in different important infrastructures. Examples include repair systems for sewer structures, where biogenic sulfuric acid corrosion is the major degradation mechanism. Low-calcium alkali-activated materials (AAMs) have been repeatedly observed to exhibit high acid resistance. However, the reasons for the high acid resistance of these materials were not fully understood until recently, and the use of highly alkaline activator solutions to produce AAMs appears to hamper their commercial uptake. These issues have been tackled by characterising one-part AAMs and studying their alteration when exposed to sulfuric acid.

Materials & Methods One-part AAMs were synthesized by mixing blends of solid silica and sodium aluminate with water, and subsequent curing at 60–80 °C [1-4]. Acid resistance testing was performed according to DIN 19573, i.e. exposure to sulfuric acid at pH = 1 for 70 days [4]. Characterisation of the cured and the acid-exposed materials was done by XRD, ATR-FTIR, SEM as well as 29Si, 27Al and 1H MAS NMR spectroscopy, including cross-polarisation and double-resonance methods [1,3-5].

Results Materials synthesized from industrial silicas were gel-zeolite composites, containing a substantial amount of unreacted 'excess' silica, while materials synthesized from rice husk ash were fully amorphous, containing 'excess' hydrous alumina [1-5]. The sulfuric acid resistance of mortars based on these binders conformed to the requirements of DIN 19573 for sewer repair applications. The high acid resistance was caused by precipitation of silica gel at the mortar-solution interface, inhibiting further degradation [4]. The presence of alumina gel may inhibit bacterial activity, potentially further improving performance in sewer environments [5].

Conclusions The phase assemblage of silica/sodium aluminate-based one-part AAMs can be adjusted via choice of the silica starting material. Properly designed materials exhibit excellent acid resistance, caused by precipitation of silica gel which protects subjacent regions, and they may also inhibit bacterial activity.

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[5] Greiser S, Gluth GJG, Sturm P, Jäger C (2018) RSC Adv 8:40164-40171

Keywords: Alkali-activated materials, One-part mix, Acid resistance

ABS 517

FIRING ENERGY REDUCING MEASURES FOR CERAMIC TILES

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Ceramic tile manufacturing process is energy intensive process and energy cost is about 30% of the total manufacturing cost. Thus, there is a great need to reduce the energy consumption and associated CO2 emission in tile industry. In this presentation, various approaches to reduce the energy consumption associated with firing will be presented for both wall and floor tiles. These will include incremental measures such as formulations of fluxes to reduce viscosity of the liquid phase and thus sintering temperatures of porcelain tiles as well as some innovative approaches such as use of boron compounds to reduce firing temperature of wall tiles. In addition, some radical approaches such as the development of new routes to make wall tiles without firing will also be discussed. With this respect, attention will be drawn on geopolymerisation technology with some promising results.

Keywords: Tile, Firing temperature, Geopolymer

ABS 487

MICROSTRUCTURAL ANALYSIS OF SALT-GLAZED POTTERY

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Two defining features of certain salt-glazed studio pottery are (i) a surface texture akin to 'orange peel', with mm-scale dimples across the ware evident to the naked eye, such as in Figure 1, and (ii) fine scale cracking of the salt glaze arising from differences on cooling from the glazing temperature between the coefficients of thermal expansion of the glaze and the underlying ceramic body. However, remarkably little is known about the reasons behind the formation and development of the orange peel effect in the kiln, and there is little quantitative information to be found in the scientific literature on the length scales due to cracking of salt-glazed pottery. In this work, salt glazes on ceramic plates and pots produced commercially by studio potters in the UK have been characterised by conventional and polarised light microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray powder diffraction in order to ascertain the thickness and composition of the glazes, the nature of any crystalline phases present and the type and scale of crack patterns observed. Particular attention has been paid to the chemical composition of the glaze as a function of position to try and establish the reason for the 'orange peel'. This is because one possible way of explaining the occurrence of this texture is that it is produced as a consequence of local chemical inhomogeneities within the glaze affecting its local viscosity, and therefore its local surface energy.

Keywords: Salt glazing, MIcrostructural analysis, Chemical analysis

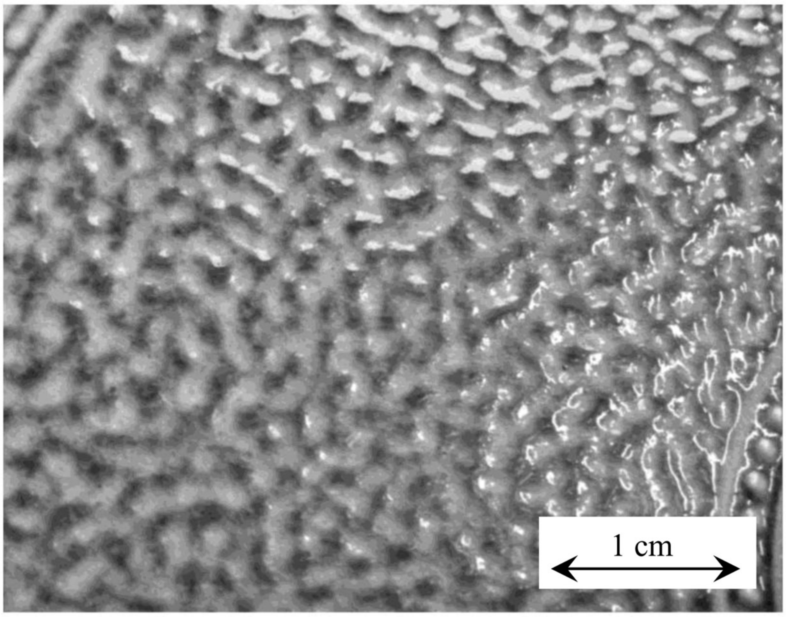

Figure 1 Example of a salt glazed surface showing 'orange peel' surface texture.

ABS 301

THE IMPACT OF MOLAR RATION OF SiO_2/Al_2O_3 ON STRUCTURE AND TECHNOLOGICAL PROPERTIES OF LIME-ALKALINE GLAZES.

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The ratio of molar SiO2 to Al2O3, in accordance with the Seger formula and Stull's diagrams, is the first parameter describing the temperature range of application of the ceramic glazes. The value of this index is also used to predict the degree of glaze's matteness, but taking into account into the molar content in the composition of alkali metals oxides and alkaline earth metal oxides.

Calcium-alkali glazes is widely used in the household ceramics industry, the technology of ceramic tile, sanitary ware and stoneware and porcelain tableware production. This work is based on the selected porcelain type of glaze from the SiO2-Al2O3-CaO-Na2O-K2O system. The test results, obtained values of technological and usable parameters and structure changes, show how important is the change in the molar ratio of silica to alumina and how the complex system are currently used ceramic glazes.

Keywords: glass-ceramic glazes, structure, silica to alumina ratio

ABS 234

GEOPOLYMER BASED HYBRID MATERIALS: STATE OF THE ART AND PERSPECTIVES

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Organic-inorganic hybrid materials play a key role in the development of advanced functional materials since the synergistic interactions between organic and inorganic components result into new, special properties, and not simply the sum of those characterizing the parent phases. Among these materials, a particularly interesting area includes geopolymer-based ones, for their application as a promising alternative to cement-based products, mainly in the field of civil and industrial constructions.

GeoSyl is an innovative hybrid material developed and patented (NA2014A000027) from a team of researchers belonging to Department of Engineering of the University of Naples Parthenope, in collaboration with the Department of Structures for Engineering and Architecture and the Department of Chemical Sciences of the University of Naples Federico II. [1,2]

GeoSyl is obtained by reacting a silicate source (i.e. fly ash deriving from coal-fired thermoelectric power plants) with mixtures of dialkylsiloxane oligomers through a polycondensation reaction that is carried out in strongly alkaline conditions. This reaction produces an amorphous hybrid material made of an interpenetrated network of aluminosilicate chains in which Si-O units derive both from inorganic and organic reactants. This structure provides to GeoSyl chemical and thermal stability, very good fire resistance, and enhanced mechanical properties. Moreover, the fine tuning of the viscosity of the reaction slurry turns out in the possibility to obtain expanded system characterized by a well-controlled porosity and low density that show high performance for thermal and acoustic insulation, while keeping excellent mechanical properties. The easy and low cost productive process used to obtain GeoSyl (both in its dense or aerated forms) can be simply adapted to a wide range of raw material, including clay muds or agricultural wastes, thus overcoming the critical drawbacks associated with raw material supply for mass production. This fact makes GeoSyl competitive, if compared to traditional binders in the concrete industry and to autoclaved aerated concretes, both from a point of view of the environmental and economic impacts. All these features demonstrate that GeoSyl is an innovative and advanced product that finds its main application in the field of energy efficiency, and could represent an appealing solution for constructing low-cost lightweight structural systems for social housing in emerging market economies.

GeoSyl is a Spin-Off of University of Naples Parthenope.

[1] G. Roviello et. al. Materials and Design, 2015, 87, 82-94. [2] G. Roviello et. al. Composites Part B, 2018, 128, 225-237.

Keywords: geopolymers, hybrid materials, energy efficiency

ABS 204

POSITIVE ENVIRONMENTAL IMPACT OF THE CERAMIC INDUSTRIES

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Ceramic tile factories consume a variety of natural resources, such as water, energy and mineral raw materials. This activity has a very positive economic-social impact, although it also generates an environmental impact that must be minimized. By using the strategies of the circular economy, it is possible to reverse this impact and generate clean water in its environment, which can be used for agricultural purposes or for the replenishment of aquifers. The technologies used for energy recovery and water purification are shown.

Keywords: Energy, water, circular economy

ABS 180

HIGH REFLECTIVE GLASS CERAMICS FRITS FOR CERAMIC GLAZES

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Over the last decades, thanks to higher environmental awareness and the increasing issues related to Urban Heat Island effect and Heat waves during hot seasons, the theme of passive cooling has attracted more attention. In particular, one of the most effective passive cooling techniques available is represented by solar reflecting materials, which reflects solar radiations in the whole solar spectrum (Uv-Vis-Nir).

From the introduction of ink-jet printers in tiles decoration, the use of porcelain stoneware for facades claddings has increased. On the other hand, because of the thickness of ink-jet decoration, it has been demonstrated how the solar reflectance performances are now closely related to the engobe properties.

In this work we have studied the crystallization of commercial and custom made frits to evaluate their behavior against solar radiation and their effect on the performances of engobes.

Seven industrial frits, having different chemical composition, were milled in water in order to obtain powders with a grain size distribution (D90) lower than 40 micron. The dried powders were pressed at 35 MPa and subsequently fired at different temperatures.

The sintered glass ceramics samples have been characterized by Differential Thermal Analysis (DTA), Heating Microscope (HM), Scanning electron microscopy (SEM), XRay Diffraction (XRD), L*, a*, b* and solar reflectance (SR). In particular SR results have been correlated with crystals size, crystallization degree and crystals' mineralogy.

Keywords: Cool Roof, Solar reflectance, Glass-ceramics

ABS 84

CLAYS WITH NO CARBONATES IN BRICK MANUFACTURING: LINK MICROSTRUCTURAL AND MINERALOGICAL EVOLUTION TO FIRING CONDITIONS

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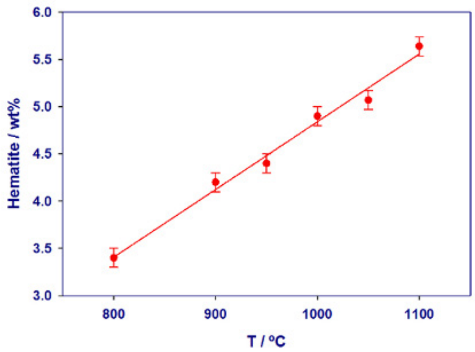
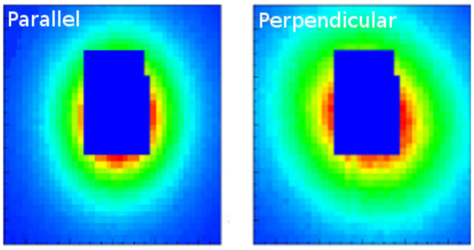
Microstructural and mineralogical evolution of the raw clay during firing is a complex process in which a series of physical-chemical, compositional and process variables, play a role.
Production bricks and raw clays employed in brick manufacturing and fired in laboratory, have been studied with a combination of analytical techniques. Observation under petrographic microscope, supported by electron microscopy, enabled for the reconstruction of the thermal history and microstructural evolution in function of the characteristics of the raw clays. X-ray diffraction with the Rietveld method (including the quantification of the amorphous fraction) allowed to propose the unit-cell parameter of spinel, the weight fractions of hematite, mullite and amorphous fraction, as indicators of maximum firing temperature through the implementation of calibration curves (see Figure below).
A similar calibration curve has been built from a structural parameter proportional to the specific surface of pores, obtained from small angle neutron scattering. The evolution of pore size distribution retrieved by this technique, which is sensitive to both close and open porosity, indicated a multiscale nature for the pore-matrix microstructure and the presence of structural anisotropy induced by the extrusion process in the direction parallel and perpendicular to the direction of extrusion (see Figure below). Domains with prevalent orientation perpendicular to the direction of extrusion were not considered previously, and are thought to form thanks to the development of laminations close to the screw blades and wings of the screw extruder. Such microstructural features impact on anisotropy of the thermal and elastic properties, and, ultimately, on the brick performance. The fractal quality of the surface area of pores obtained from small angle neutron scattering is also a very sensitive microstructural parameter, allowing for distinguishing bricks produced from different raw clays.
The results may have implications for improving the process variables in manufacturing, for the production of custom made replacement materials in the conservation of cultural heritage or for the characterization of the manufacturing process of archaeological fired-clay objects.

Keywords: Fired clay bricks, X-ray diffraction, small angle scattering





ABS 958

QUALITY OF PRECURSORS AND NANOSTRUCTURAL EVOLUTION OF SILICATE BINDING PHASES IN SLAG-FLY ASH-METAKAOLIN-BASED BINDERS

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Slag-fly ash, and slag-metakaolin binders are two types of room temperature hardening binders that have excellent mechanical properties and significantly lower carbon footprint than OPC. C-N-A-S-H gel and geopolymer are the binding phases in these binders. The aim of this study was two-fold. The first aim was to evaluate the quality of precursors (slag, metakaolin, and fly ash) using MAS-NMR, FTIR, XRD, XRF, and laser diffraction. The second aim was to monitor the structural changes of the binding phases with increasing time, temperature, and slag/fly ash ratio. This was achieved by using selective chemical extractions and nuclear magnetic resonance (MAS-NMR). Using 27Al MAS-NMR the proportion of four-, five- and six-coordinated Al in precursors were determined. The structure of C-N-A-S-H gel and geopolymer at various times, slag/fly ash ratios, and curing temperatures were determined using 29Si MAS-NMR. A “soft gel” was formed during setting in slag-fly ash binders. The structure of this “soft gel” which had a solid percolating network but could not bear load was put forth. FTIR was used to corroborate the results of MAS-NMR.

Keywords: Geopolymers, Alkali activated cements, Slag-Fly ash binders

S08

SILICATE CERAMICS

ORAL PRESENTATIONS

ABS 859

VALORIZATION OF WOODEN FURNITURE WASTES TO IMPROVE THERMAL INSULATION OF FIRED CLAY BRICKS

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Thermal regulation requirements for buildings have become an important issue, especially since the enactment of the law n° 2015-992 (17th of August 2015) presenting the energy transition strategy of the French state. This new regulation implies developing energy efficient buildings in order to decrease primary energy consumption of fossil energies. In this context, improving thermal insulation of building materials will provide economic and environmental benefits.

The following project aims at improving thermal insulation of fired clay bricks through addition of wooden furniture wastes. This project consists in (i) developing, by extrusion process, innovative “lightweight” bricks with low thermal conductivity and mechanical properties compatible with current norms on building materials and (ii) opening a new outlet of valorization of wooden furniture wastes. The wood waste was mixed, after grinding, as a pore former, with raw clay materials in suitable proportions to obtain a homogenous and plastic paste. Furthermore, based on the type, shape and size of wooden furniture waste, anisotropy induced by the extrusion process was investigated.

The effect of the nature and the amount (5 or 10 wt.%) of wooden furniture wastes on the properties of the final porous fired brick prepared by extrusion was assessed though measurements of mass loss, drying and sintering shrinkage, porosity, bulk density and thermal conductivity. Results showed that incorporation of wooden furniture waste into the clay mixture yielded increase of porosity after firing and hence decrease of thermal conductivity. For example, addition of 10 wt.% wood waste yielded a pore volume fraction of 45% with a conductivity of 0.6 W.m-1.K-1. Moreover, due to orientation of (i) the clay platelets and (ii) non-isometric pores, the effect of anisotropy was significant. Concerning the thermal conductivity, the anisotropic ratio ranged from 1.14 to 1.47.

The addition of wooden furniture wastes in the basic matrix of clay brick enabled a significant improvement of the thermal insulation of fired clay bricks. Ongoing work aims at measuring the mechanical properties of the porous clay bricks in order to assess their possible use as load-bearing building materials.

Keywords: Thermal insulation, Wooden furniture wastes, Fired clay bricks

ABS 850

ACTIVATING SCHIST TYPE MATERIALS AS A CEMENT SUBSTITUTION

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Supplementary Cementitious Materials (SCMs) are replacing Ordinary Portland Cement (OPC) in binder formulations with a positive impact on reducing the CO2 emission produced by global cement industry. Conventional types of SCMs like fly-ash or slag materials utilized in cement industry contain a high amount of silica (SiO2). Such SCMs are of limited availability. An alternative to these waste products is to use clay containing materials such as kaolinite. Kaolinite is used as an SCM after being activated through controlled calcination process that forms a very reactive material known as meta-kaolin (MK). MK is a semi-amorphous alumina silicate. Several studies suggested that limestone and MK could be used as a proper cement substitution, showing a higher strength development than pure Portland cement. In this study, two schist type materials (M1 and M2) with similar phase compositions were provided by a local mine. Calcination of these materials to activate the clayey phases were performed in a temperature range from 500 to 900C. The temperature range was selected in relation to the start and end of the decomposition reactions of the samples. The degrees of activation were measured through the weight losses of samples as they decomposed through de-hydroxylation reactions. Samples were activated to 30, 50, 80 and 100wt% of their total weight losses. Phase compositions before and after the heat treatment were analyzed with the help of X-Ray Diffraction (XRD) analysis. Activated M1 and M2 samples were incorporated into cement paste formation in a ratio of 30wt% to investigate their performance in strength development over hydration duration. Strength development of substituted pastes was evaluated with compressive strength measurements after 2, 5, 7, 28, 50 and 90 days of hydration. Samples prepared with activated kaolinite were used benchmarking tool. Best strength development results were obtained with M1 samples activated at 80% of its total weight loss. The difference in strength development between M1 and M2 samples illustrated the importance of phase composition in the schist mines.

Keywords: Pozzolanic Reaction, Supplementary Cementitious Materials (SCMs), Calcined Clay, Kaolinite, Schist Type Materials, cement substitution, calcined clay cement, schist type materials

ABS 844

HIGH SHEAR RATE VISCOSITY MEASUREMENTS OF CERAMIC INKS BY VISUAL MICROFLUIDIC RHEOMETER

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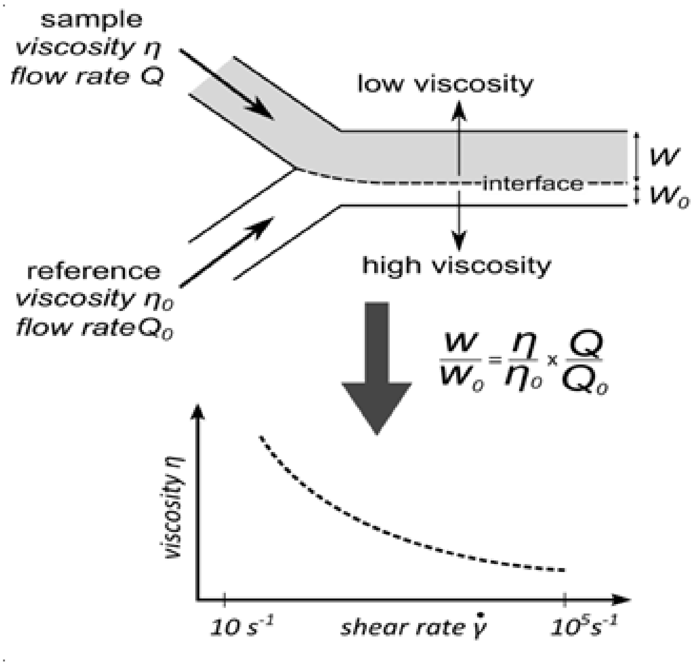
Introduction Understanding rheological behavior of inks is a guarantee of high-quality results and limiting process issues like ink splashing, bleeding and clogging of the printing head. FluidicamRHEO is designed for viscosity measurements of products from very fluid to thick formulations as a function of shear rate (up to 10^5 s-^{1}) and temperature, allowing quick and accurate ink characterization under real process conditions.
Materials and methods: FluidicamRHEO is a microfluidic based instrument, allows to measure viscosity as a function of shear rate and temperature in a single experiment set-up. Using a small sample volume, the technology allows flow viscosity measurements of low viscosity samples in a wide range of shear rates (up to 10^5 s-^{1}). During the measurement, a sample and a viscosity standard are pushed together through a microfluidic chip (Y-junction) at controlled flow rates. Images of the resulting laminar co-flow are acquired with a digital camera and the position of the interface is measured. The interface position is related to the ratio of flow rates between the sample and the reference allowing determining the viscosity.
Results This work shows the results of several ceramic inks with different formulations (dispersants, concentrations…) analyzed over a large range of shear rates not available with standard rotational rheometers and at operating temperatures of the process. FluidicamRHEO ranked the tested ceramic inks with small viscosity differences around 0.5 mPa.s depending on the type of solvent tested, the type and the concentration wt% of the dispersion, the type of dispersant and many other compounds of the inks. The instrument is suitable for high shear characterization of the rheological behavior of different formulation of ceramic inks in a short amount of time.
Conclusion FLUIDICAMRHEO allows viscosity assessing in real process conditions of operating shear and temperature to improve the printing quality. The instrument provides accurate viscosity measurement with less than 2mL sample volume for a flow curve over a large range of shear rates in less than 3 minutes analyzing time. Thus, the confined microfluidic system of Fluidicam provides accurate viscosity measurements without solvent evaporation or dying issues.

Keywords: inkjet inks, ceramic inks, rheology of inks



ABS 841

ECO-FRIENDLY BRICKS MANUFACTURED WITH CONSTRUCTION AND DEMOLITION WASTE (CDW)

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Construction and demolition waste (CDW) is a worldwide problem. In EU-28 this kind of waste constitute the 35% of the special waste produced. In general, CDW mineral fraction is very heterogeneous (mortar, ceramics, concrete, rocks, natural gravel, masonry, sand, soil, etc.) and depends on the characteristics of each construction. For a suitable recycling it is necessary to separate specific materials as plastic, timber, soil, plaster, composites, paints and dangerous substances as mercury, lead or asbestos. The CDW hazardousness depending on the content these dangerous substances.

The European Directive 2008/98 foresees that in 2020 is reached 70% of CDW recycling. In line with the legislation, this study proposes the recycling of three different CDW (from tiles, cement and bricks) into a commercial brick body by total substitution of the sand. The recycled aggregates were physical and mechanical pre-treated in a plant and showed a particle range 0-4 mm.

A commercial brick body (90 wt% clay /10 wt% sand) was used as reference and the mixes were prepared substituting completely of sand by the recycled aggregates. Brick samples were extruded with variable water amount (20-22%) in order to obtain a suitable plasticity. Then, dried for 12hs at 105°C and fired in an electrical furnace (thermal cycle: 10 h; Tmax: 1020°C and isotherm: 2.5 hs) simulating a typical brick making process.

The specimens were characterized following the technical rules. In particular, linear shrinkage (LS%) and flexural strength on dried green pieces and (24h-immersion) water absorption (WA%), linear shrinkage (LS%), flexural strength, colour test, efflorescence and Hg-porosimetry on fired pieces.

The brick samples with recycled aggregates as received showed an increase of “calcinelli” respect to the reference. For this reason, further experiments were conducted using the aggregates sieved below 1mm. For these mixtures the defect was eliminated. Regarding the tests after drying the recycled aggregates provoke a slightly decrease in LS% values while the cement sand improves the mechanical resistance in green.

Fired bricks showed LS% and WA% values similar to the reference and an improvement of flexural strength (up to 18%). Mercury intrusion porosimetry tests highlighted a slightly increase of total porosity except for samples prepared with cement sand. Besides, from aesthetical point of view using CDW the efflorescence is decreased. Finally, on the basis of the results obtained, the recycled aggregates studied can certainly use to replace natural sand.

Keywords: Bricks, Construction Demolition Waste, Recycled Aggregates

ABS 835

MODIFICATION OF THE GEOPOLYMERS VISCOSITY AND MECHANICAL PROPERTIES

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The French national radioactive waste management agency (Andra) is in charge of assessing the long-term safety for a radioactive waste disposal in deep geological medium. In the purpose of using a lining for high level waste, a tubular shape is required. Among various materials, geopolymers are promising to be studied in this context. The rheology of mixture as well as the mechanical strength of the consolidated material must be investigated to control the final product. The aim of this work is to appreciate the impact of mineral additives on the rheology and mechanical strength of geopolymers.

To control the formulation, the metakaolin amount, the nature of the activation solution and various additives have been investigated to enhance the physical properties. The rheology data (viscometer), the microstructure (SEM) and the compressive strength values have been compared.

The nature of the solution, the metakaolin amount and the addition of charge allow to change the initial viscosity and the setting time of the reactive mixture. The compressive test has shown that the composition of the geopolymer and the addition (nature and charge) can increase maximum compressive strength and modify the failure behavior from fragile to ductile.

The viscosity of the reactive mixture and the mechanical properties of the geopolymer can be controlled and adapted changing the composition and the nature and charge of mineral additives.

Keywords: Geopolymer, Viscosity ,Mechanical Properties

ABS 811

WASTE-DERIVED GLASS-CERAMICS FIRED IN NITROGEN: STABILIZATION AND FUNCTIONALIZATION

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Fine glass powders, mostly deriving from the plasma processing of municipal solid waste (‘Plasmastone’), had been already successfully converted into highly porous foams by alkali activation, mechanical stirring of suspensions and sintering at 800-1000 °C, in air. The stabilization of pollutants was achieved only by mixing Plasmastone with 30 wt% boro-alumino-silicate glass, in turn deriving from the recycling of pharmaceutical vials; common soda-lime glass, although helpful in controlling the sintering and crystallization of Plasmastone, did not lead to chemically stable products. The research here presented was essentially conceived for overcoming the difficulties in the stabilization of pollutants, by firing in nitrogen. The change in the atmosphere had a significant impact on the $Fe2+/Fe3+$ balance, leading to a different phase assemblage, in turn connected with the stabilization of pollutants even operating with soda-lime glass, at only 800 °C. The formation of magnetite ($Fe3O4$) made the obtained glass-ceramic foams particularly interesting as functional materials, based on the observed electromagnetic shielding effectiveness.

Keywords: Glass-ceramics, Alkali activation, Shielding effectiveness

ABS 805

DEVELOPMENT OF A CERAMIC COLOURED GLAZE CONTAINING ZIRCON AND STUDY OF THE EFFECTS ON SOLAR REFLECTANCE INDEX (SRI)

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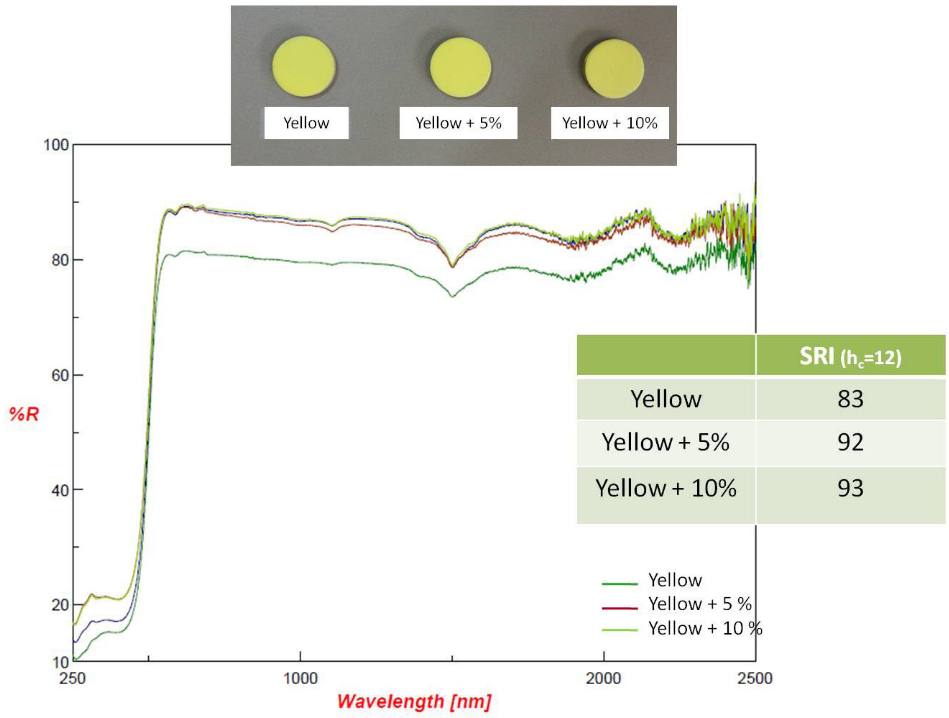
Objective A building envelop with improved energy performances can be obtained by using ceramic tiles with high solar reflectance able to reduce the urban heat island effect. The aim of this work was to study the addition of zircon as opacifier, in several ceramic coloured glazes, in terms of Solar Reflectance Index (SRI) and thermal performances.

Materials & Methods Ceramic glazes (white, yellow, blue, brown, green and black) were prepared by adding zircon ($ZrSiO4$) to the mix composition (0 wt% as reference, 5 wt% and 10 wt%). These 18 glazes were applied on ceramic tiles and fired in an electric furnace at 1180°C. Fired tiles belongs to class BIa following the standard classification (EN 14411), having a water absorption below 0.5%.

Samples were analysed in terms of solar reflectance spectra and thermal emissivity in order to calculate the SRI values. The colour of the samples was determined according to the Commission Internationale de l'Eclairage (CIE). The thermal performances were also evaluated by monitoring the surface temperature during the summer period.

Results Results showed that the addition of zircon produces, in general, an increasing of SRI values in all the glazes. The higher SRI values are linked to the increase of the colorimetric coordinate L*, related to the lightness of the colour, but also to the increase in spectral components in the NIR range (780-2500 nm). Results of yellow glaze are reported in the figure.

Results of the summer monitoring showed that by comparing the same colour, the glazes containing zircon (with higher L* value and higher SRI) remain cooler.



	SRI (h_c=12)
Yellow	83
Yellow + 5%	92
Yellow + 10%	93

Conclusions The tests performed on the glazed ceramic tile samples allowed to point out that, in general, the addition of zircon increases the solar reflectance property of the glazes.

As the percentage of zircon added in the glaze increases, the value of SRI increases linearly for all the colours analyzed. Incidentally, the whitening effect of zircon is also highlighted by the linear increase in the colorimetric coordinate L*, linked to the lightness of the colour. Moreover, excluding the colour appearance, the improvement of solar reflectance property, in terms of reducing surface temperatures, is observed in those glazes with higher spectral curves in the NIR range, in particular after 1500 nm. The increase of spectral values in the NIR range is an effect that correlates the addition of zircon in the glazes. Thus, zircon can act as a cooling addition to the composition of the ceramic glaze.

Keywords: Zircon, Ceramic tiles, Solar Reflectance Index

ABS 791

EFFECT OF POZZOLANIC ADDITIVES ON HYDRATION PECULIARITIES OF PLASTICIZED OR NOT PLASTICIZED LIGHTWEIGHT REFRACTORY MATERIAL CONTAINING EXPANDED GLASS FILLER

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Lightweight refractory plaster with expanded glass (EG) additions is an innovative material that could be used as a durable and lightweight composite material to protect external structures of energy equipment. To enhance the performance of lightweight plaster with EG aggregate and reduce its density, the following pozzolanic additives were used: metakaolin and glass mixture (M) from EG manufacturing and microsilica (S). The aim of the paper is to determine the effect of mixed pozzolanic waste materials on hydration peculiarities of lightweight refractory plaster with or without plasticizers and plaster containing expanded glass filler.

Calorimetry tests (V/K=0.35, 48h) of refractory mixes with EG and two types of pozzolanic additions were conducted. Mixes with other deflocculants were also tested. The following trends were observed in the analysis of obtained relationship curves:

1. FW plasticiser causes earlier hydration of the mix; however, the total heat released is slightly lower compared to the control specimen. A flash of early (hydration) heat was observed in the mixes with this addition. Addition M used in these mixes does not have any effect on hydration rate. The amount of early hydration heat is the same as in control specimens and the total heat released is very similar.
2. FW plasticiser retards the hydration of the mix; the total heat released is also lower compared to the control specimen. It was noticed that the induction period in the mixes with chemical addition is longer. Addition M (5%) used in these mixes has an effect on hydration rate. The amount of early hydration heat is higher compared to control specimens without the pozzolanic additions, the total heat released is also higher.

Tests into physical and mechanical properties showed that when a part of milled expanded clay is replaced with the above-mentioned pozzolanic additives (with different plasticizers), the density after setting and thermal treatment (at 110°C, 600°C and 800°C) reduces 10% – 15% compared to the control specimen, compressive strength values range from 7 to 3MPa, and flexural strength values range from 2.5 to 1MPa. It should be noted that specimens of all compositions shrink slightly in 600°C–800°C temperature ranges. Physical and mechanical characteristics obtained lead to the conclusion that such a material could be used for the protective layer in energy equipment where operation temperatures are <800°C.

Keywords: lightweight refractory materia, pozzolanic additives, expanded glass

ABS 753

DEVELOPMENT OF A COLORED STONEWARE PASTE THROUGH THE VALORIZATION OF AN INDUSTRIAL WASTE

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The modern view on the exploitation of natural resources and its availability led to changes in policies and the development of more interconnected industrial systems. Circular economy embodies such philosophy perfectly since the byproduct/waste of one industry is used as raw material in other. This brings environmental and economic benefits, since it is possible to save on the consumption of virgin raw materials, add value to a byproduct/waste while avoiding disposal related costs. Of course, such valorization only makes sense if in the end a product with the required properties is obtained.

In this work, a colored stoneware paste was developed through the valorization of an industrial waste – a galvanizing sludge. The sludge was incorporated, in different proportions, in the ceramic paste, in the as-received condition and after calcination. The final product was characterized in terms of water absorption, flexural strength, color (CIEL*a*b* coordinates), thermal expansion coefficient and thermal shock resistance. Leaching tests were also carried out to evaluate the levels of lead, cadmium, nickel, and chromium leached. The optimized ceramic products have the intended visual appearance and, at the same time, the required technical properties.

Acknowledgments
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Keywords: stoneware paste, industrial waste, valorization

ABS 222

EFFICIENT USE OF NEPHELINE SYENITE AS A FLUXING AGENT IN INDUSTRIAL CERAMIC FORMULATIONS

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Feldspar and clay minerals are employed in ceramics industry as a raw material. Apart from these, feldspathoid (especially nepheline syenite) group minerals are commonly preferred in formulations. Nepheline syenite is a quartz-free aluminum silicate complex rock consisting of different mineral phases such as nepheline, alkali feldspar, and biotite.Because of its extremely low melting point and high alumina content, nepheline syenite is used as a glass phase promoter, a ceramic flux and also as a functional filler in paint, plastics etc. Like Feldspar, nepheline syenite is used as a flux in tile, sanitaryware, porcelain, vitreous and semi-vitreous bodies. It provides high alumina without associated free silica in its raw form and fluxing oxides to form silicates with free silica in bodies. This stabilizes the expansion curve of the fired body. It is also an excellent filler and flux, especially for fast firing conditions. Nepheline syenite is valuable in glass batches to achieve the lowest melting temperature while acting as a source of Alumina.

Buzlukdag nepheline syenite from Kirsehir represents one of the largest and unaltered alkaline intrusive body in Central Anatolia region of Turkey. Main mineral composition is nepheline (15-35 wt. %), K-feldspar (orthoclase) (41-69 wt. %), albite (25-37w. %), biotite (0.3-2.5 wt. %). Buzlukdag nepheline syenites have K2O/Na2O and Na2O/K2O ratios between 0.44-1.5 wt. % (mean 0.60 wt. %) and 0.89-2.66 wt. % (1.53 wt. % on average) respectively, thus they are very suitable for ceramic and glass industries.

In this study, potential use of Buzlukdag nepheline syenite was examined as fluxing agent in place of albite in ceramic tile and ceramic sanitaryware bodies. The rheological behavior, energy efficiency and its effect on technical properties of the representative bodies were examined detail.The results showed that, with the use of nepheline syenite in the body formulations, sintering behavior and technical properties as water absorption, deformation,breaking strenght were affected positively.

Keywords: nepheline syenite, ceramic

ABS 720

DEVELOPMENT OF ZEOLITE BASED BRAKE PADS FOR BRAKE DISC TECHNOLOGY

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In the brake disc technology, during the braking the kinetic energy of the vehicle is converted into heat by friction, when the calipers squeeze a pair of pads against the brake rotor.

Brake pads are composite material reinforced with metallic and inorganic fibers. Lubricant and abrasive are used to have the optimal friction properties. Brake pads are organic based composites and the phenolic resin is the most used type of matrix.

Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon and oxygen in their regular framework. Zeolites are generally formed in strong alkali solution (Na, K) and in hydrothermal conditions. Considering their inorganic structure, zeolite-based composites have better thermal properties than organic resins, which typically decompose by oxidation starting from ~400°C.

In this work, zeolite-based brake pads were produced using an innovative approach, where kaolinite and sodium hydroxide were directly converted into a zeolite structure through an hydrothermal synthesis without the addition of any water, and therefore in dry conditions, so without any modification on the process production of phenolic-based brake pads.

XRD analysis was conducted to confirm the formation of the desired zeolitic phase.

The optimization of the brake formulations has been done, on the base of physical properties and friction characterization of geopolymer based brake pads.

Keywords: brake pads, geopolymers, dry process

ABS 719

SINTERING BEHAVIOR OF WASTE-BASED PORCELAIN STONEWARE BODIES

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The production of ceramic tiles is continuously increasing worldwide, implying a growing demand for raw materials. On the other hand, the progressive depletion of the main feldspathic flux deposits is forcing the ceramic industry to search for suitable substitutes. Although the tile-making industry proved to be able to recycle its own processing residues into cannibalistic loops, the use of wastes from further sources is at present quite limited. The use of glassy wastes, for instance, is usually hindered by technological reasons: a low-melting glass can significantly affect the firing behavior and particularly high temperature permanent deformations. Besides a general convergence towards a “fluxing effect” of waste glasses, it is not yet clear what is their influence on the amount, composition and physical properties of vitreous phase as well as on the sintering. The main goal of this study is to assess the firing behavior of porcelain stoneware bodies containing glassy wastes. Six different sources (bottle, PC-TV screen, lamps, glaze manufacturing, ceramic tile processing and porcelain stoneware grinding) provided wastes to a large extent glassy in nature that were added separately in increasing amounts, 20-40-60%, to a reference body up to a complete substitution of feldspathic fluxes. The quantitative XRPD analyses (by Rietveld method) revealed that additions up to 40% kept the amount of liquid phase close to classic porcelain stoneware (60-75%). Nevertheless, an improved sintering kinetics was observed with lower temperatures of maximum densification (1060-1080°C vs. 1190-1220°C). The liquid phases existing at low temperatures have a peculiar composition, due to both the waste glass contribution and the strong dissolution of mullite and quartz. The residual quartz present in the waste-bearing fired bodies (7-11%) is much less than in the reference body (22%). This implies a loss of solid load that could be ascribed for a permanent deformation of the ceramic slab. On the other hand, melting of quartz increases the SiO2 content in the liquid phase, which in turn increases the melt viscosity, being silica a glass network former. An opposite mechanism characterizes feldspars. These two antagonistic phenomena determine the equilibrium between feldspars and quartz – i.e., the solid load – and the melt: a decreasing viscosity of the ceramic body (caused by crystalline phase dissolution) can be damped by a viscosity boosting of the liquid phase (stemming from an enrichment of glass network formers) or fostered by a viscosity drop due to feldspar melting.

Keywords: glassy wastes, porcelain stoneware, sintering

ABS 693

INFLUENCE OF ACTIVATOR RATIO ON THE HYDRATION PROCESS OF GROUNDED BLAST FURNACE SLAG

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Blast furnace slag presents a latent hydraulicity, meaning that under specific activation conditions it can dissolves and leads to formation and growth of calcium silicate hydrates similar to those observed after hydration of Portland cement. Slag is an industrial waste that can be used as a partial or total substitute of cement, therefore reducing greenhouse gas emissions contribution. Nonetheless an activator has to be added to slag in order to trigger its hydration. This activation can be calcic, sodic or sulfatic and usually involves a pH value above 12.5.

In this work, the influence of the activator to slag mass ratio on the hydration process of slag was studied. Two different activators were used: sodium hydroxide (NaOH) and calcium sulfate anhydrite (CaSO4). The former is commonly used to set off slag hydration, the latter has been shown strengthen mechanical properties after hydration, both being produced at low cost. In the two cases, activators samples were prepared with a water to slag ratio equal to 0.4 and activator to slag mass ratios of 1.25; 5; 10; 15 and 20 % respectively. Hydration kinetics were followed in situ during 3 days by Fourier transformed infrared spectroscopy (FTIR) in attenuated total reflectance (ATR) mode, using a time step of one minute. Activated slag samples were unmolded after 24 hours and conserved in tightly closed plastic film for wet cure until being characterized using several techniques at 24 hours, 1 day and 28 days: mechanical strength in uniaxial compression, microstructure description by FTIR, X-ray diffraction (XRD) and scanning electron spectroscopy (SEM) with energy-dispersive X-ray spectroscopy measurements (EDX). The aim of these observations was to link nature and amount of activator to physico-chemical properties and microstructure of the hydrates formed. A minimum of 5 % of activator was needed to trigger consolidation and hardening of the samples within the first 24 hours. In situ infrared measurements showed that hydrates formed were mainly calcium silicates and calcium aluminates. XRD measurements brings out also the presence of an amorphous phase mainly composed by the hydrates gel-like structure. An increase in activator to slag ratio logically led to an acceleration of hydration kinetics.

This work shows how the use of different activator modifies the hardening kinetics, the microstructure formed and the associated mechanical properties. This study was conducted as part of a more general project dedicated to the formulation of an earth based concrete stabilized with activated slag.

Keywords: Slag hydration, Activator content, Calcium sulfate

ABS 676

WASTE RECYCLING IN CERAMIC TILES: A TECHNOLOGICAL OUTLOOK

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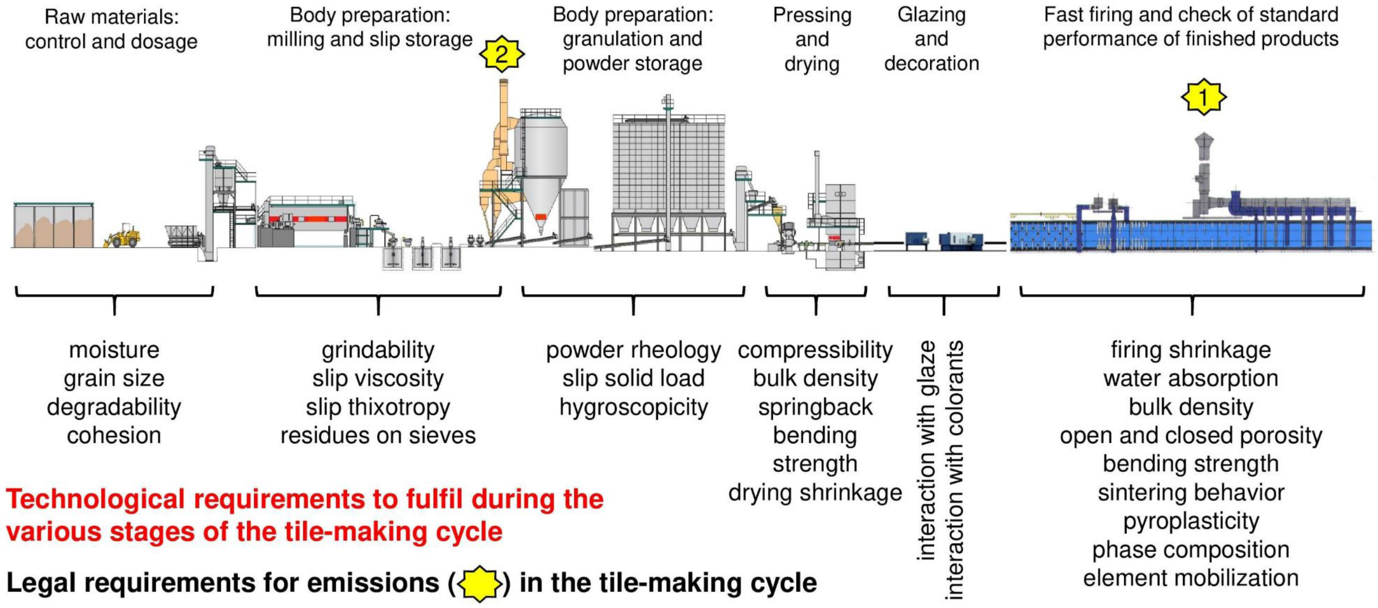
The ceramic tile industry has been facing new environmental and economic challenges that urge on improved sustainability through the transition towards the circular economy. Within this framework, efforts are mainly spent for waste recycling, which is the main "R" action that can be implemented at various levels in the ceramic industry. For this purpose, the resource efficiency can be enhanced along the manufacturing process (cannibalizing in-house residues) or the value chain (recycling residues from other ceramic productions). In addition, wastes from further sources (municipal wastes and residues from other industrial sectors) should be utilized under a systemic approach. Despite the relatively large body of literature, an obstacle to waste recycling in tile-making is the lack of information about the repercussions on process and product features. The goal is to critically overview current knowledge on waste recycling in ceramic tiles, with emphasis on both technological behavior and actual waste inertization in finished products. A large range of sources was considered: sorting of municipal wastes and WEEE (glasses), energy production (coal and biomass ashes), mining residues, industrial manufacturing (steel-making, foundry, ceramics, etc), construction and demolition wastes, wastewater treatment (sludges) and so on. Physical state and composition of wastes were filed together with their behavior during milling, granulation, pressing, drying, glazing and firing, once incorporated into ceramic tile bodies. Pros and cons of recycling were assessed for every type of waste, highlighting the main technological and environmental issues. Waste inertization turned to be a key point – often neglected in previous studies – that requests different strategies for porous and vitrified bodies, as hazardous elements must be firmly incorporated into new formed phases, either crystalline or vitreous. The outcome is a technological profile remarking, for each kind of waste, the suitability for ceramic tiles from the technological point of view, the recommended recyclable amount and possible missing information for a full comprehension of recycling potential.

Keywords: ceramic tiles, technological behavior, waste recycling



ABS 648

HIGH REFLECTIVE CERAMIC ENGOBES FOR INK-JET COOL ROOF GLAZES

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Ceramic based materials are recognized as a valid solution for passive cooling techniques thanks to their high thermal emissivity and the high values of solar reflectance that they can reach.

The architecture of a glazed porcelain stoneware tile is closing resembling the structure of a three layer cool roof as proposed by literature. This study is aimed, then, to optimize the NiR reflecting basecoat, that can be identified with the engobe, through the variation of frits with different chemical composition, as well as the variation of the thickness of the engobe itself. The use of ink-jet printing, moreover, decreasing the amount of ink applied on the tiles, allow the creation of reflective tiles characterized by interesting values of solar reflectance.

Porcelain stoneware substrates were coated with different engobes characterized by the presence of high reflective glass ceramics. This is aimed to increase the solar reflectance of the substrate in order to improve the solar performance of the decored tiles.

On the engobed tiles several ink-jet printing décor were applied in order to analyze the performance of the most used pigments for external application, applied with different printing conditions with and without top coat glaze. On the samples produced, together with microstructural and mineralogical characterizations, solar reflectance measurements will be performed according to ASTM E903 standard test method. The most promising samples were, moreover, subjected to accelerated aging protocols according to ASTM D7897 standard test method, which simulate 3 years of natural exposure in 3 days in the laboratory, to understand the behavior of these new products against time.

Keywords: Engobe, Solar reflectance, Ink Jet

ABS 646

APPLICATION OF NEURAL NETWORK FOR THE BEST VOLCANIC ACTIVATED MATERIALS FORMULATIONS

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Etna volcano has available huge quantity of volcanic products, such as volcanic ash and paleo-soils, both characterized by a high amorphous content (volcanic glass). The paleo-soils, locally named with the term ghiara are unique in the world and are characterized by an intense reddish color. The use of ghiara in mortars during XVII-XVIII centuries induces a higher hydraulic module than volcanic ashes, due to the physical and chemical transformations caused by the contact with the lava flows (Belfiore et al., 2010).

In the last decade, volcanic materials, in particular volcanic ash, have been tested to be used in alkali activated materials production due to their high aluminosilicate and amorphous content. Nevertheless, these materials have low reactivity and so they require thermal treatments to enhance mechanical properties and reduce the long setting time (Kameau et al., 2009; Tchakoute et al., 2013). Therefore, we prepared many formulations using these volcanic materials with different alkali ratio and mixture. In particular, we added different percentage of metakaolin (5-25%) (Diobo et al., 2014, Kani and Allahverdi 2009; Tchakoute et al., 2012, Robayo-Salazar et al., 2016) to avoid the thermal treatments on raw materials and alkali activated materials. In addition, we distinguished the two mechanic-synthesis techniques used to activate the process (in both cases mixing for 20 minutes): i) use of mill with porcelain jar; ii) or mechanical agitator.

With the aim to estimate the best formulation process for these low reactive materials, we applied the Neural Network model using the more important parameters for the formulation of geopolymers (quantity of matrix; amount and type of activators; thermal treatments) and the chemical stability (integrity test performed seven days after alkali activation) and stress resistance of the obtained products.

The results of our study showed that the application of Neural Network model is a very promising method for the research of the best alkali activation process and the right ratio between powder and activators.

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Keywords: volcanic activated materials, neural network, characterization

ABS 639

ENHANCED CORROSION RESISTANCE BY INTRODUCING NANO-SIZED INTRACRYSTALLINE PORES

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The exploitation of lightweight wear lining refractories has gradually become an important research hotspot of the refractory industry. The key challenge in the development of lightweight wear lining refractories lies in achieving guaranteed resistance against slag corrosion. In this study, lightweight alumina, magnesia and bauxite containing intracrystalline pores of 100-300 nm were obtained. Due to the small pore size of lightweight materials, the expected phase is more easily supersaturate, precipitation and ripening at a high rate, and a continuous isolation layer would be formed to prevent lightweight materials from further slag corrosion. Hence, compared to the common materials, the lightweight materials showed improved slag resistance performance.

Keywords: slag corrosion, lightweight materials, nano-pores

ABS 621

INVESTIGATION OF POSSIBLE USE OF THE BIGA PENINSULA (NW ANATOLIA) ZEOLITIC TUFFITES IN PORCELAIN TILE PRODUCTION AS AN ALTERNATIVE FLUXING AGENT

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Increasing of porcelain tile production in ceramic industry caused the more usage of feldspar minerals as fluxing material. The increase in raw material costs led to the ceramic tile producers to look for local alternative fluxing alkaline raw materials. In this context, the geological, chemical, mineralogical and technological features of the Biga Peninsula zeolitic tuffites were investigated.

Biga Peninsula zeolitic tuffites crop out within the Eocene flysch succession as the green colored horizons. Tuffites are hard and brittle, and look like marn-shale. XRD analysis revealed that they consist mainly of clinoptilolite (zeolite), montmorillonite, quartz, K-Feldspar, dolomite and muscovite minerals. The dominant minerals are clinoptilolite (> %40), quartz (%23), montmorillonite (%12) and K-Feldspar (%10). The chemical composition and thermal behavior of the tuffites were examined by XRF and DTA methots, respectively. Following the characterization issues, zeolitic tuffite was used in body recipes as %10, 30, 30 and 40 proportions instead of the alkaline raw materials (i.e. feldspars). New recipes were fired and its technological features such as firing shrinkage, water absorption and color (L, a, b) values were measured. Additionally, sintering behavior, new formed phases in fired bodies and their microstructures were investigated using by non-contact dilatometer, XRD and SEM imaging.

As a result, in the production of porcelain tile/glazed granite, Biga peninsula zeolite tuffites have been determined as an alternative fluxing material which can replace in different rates instead of conventional alkali raw materials.

Keywords: Zeolite, Fluxing agent, local raw material

ABS 620

A COMPARATIVE STUDY OF PHYSICAL PROPERTIES OF GYPSUMS AS A MOULD MATERIAL IN SANITARYWARE INDUSTRY

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Gypsum products are one of the most widely used materials in sanitaryware industry as a mould compound. The wide use of plaster of Paris has motivated a number of manufacturers to introduce different brands of the profession but their physical and mechanical properties are still questionable. The aim of the study is to access, compare and evaluate the physical properties of different plaster moulds available in Turkey sanitaryware industry. Certain gypsums were selected for the comparison of their particle size, setting time and mechanical properties with different water content. Relationships between the processing conditions, microstructure and final properties of the plaster moulds were investigated. The results showed that the rheological behaviour and the time during which the plaster suspension is pourable for making moulds were dependent on the preparation conditions. Chemical composition, particle size and water content of the mould and preparation conditions effect the performance of the moulds (pore size and distribution, microstructure, setting time, water absorption of moulds). Results showed that using the high initial viscosity and optimum water content of the plaster suspension achieved less pores and higher mechanical strength. The present study shall be able to provide some beneficial information regarding their quality control and guide the end user for improving the standardization.

Keywords: sanitaryware, gypsum mould, rheology

ABS 599

GEOPOLYMERIC 3D-PRINTED STRUCTURES WITH ZEOLITES AND ACTIVE CARBON FOR WATER PURIFICATION

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With the increase of industrial development, the world's available drinking water is more and more susceptible to contamination due to industrial wastes. To overcome this problem, it is necessary to develop effective advanced water treatment in order to remove these contaminants. Geopolymers (GPs) are widely known for its cation exchange ability and are being increasingly used for advanced water treatment to remove specific contaminants. For this reason GPs are also being considered as anion exchange materials, so they can also remove anionic compounds, especially the ones deriving from industrial waste waters. For this purpose, this work aimed to produce geopolymeric 3D printed structures with the addition of zeolite and active carbon powders in order to increase the geopolymers' capacity of ion exchange and, hopefully, remove anionic contaminants from water. Active carbon and zeolites are widely used for advanced water treatment, however they are subjected to early saturation. Thus, their presence into the geopolymeric 3D printed structures, in addition to increase the anionic exchange of the materials, could also increase their durability. For this work, two types of geopolymeric structures were produced: one with the addition of zeolite and another with active carbon; these additives were used as fillers to provide a proper viscosity to print. Both structures had the same molar ratios: Na2O/SiO2 = 0.263; SiO2/Al2O3 = 3.8; Na2O/Al2O3 = 1; H2O/Na2O = 13. In both cases, 5% of poly (ethylene glycol) with a molecular weight of 1000 g/mol (PEG 1000) was added to the slurries to give a pseudo plastic behavior to the suspension. For the ink, the Na based activating solution was added to the PEG 1000 and was mechanically stirred until the PEG was completely dissolved. To this solution, 40% of the fillers, zeolite and active carbon, were added for each ink. After stirring, metakaolin was added to the suspension, until a high viscosity ink was formed. Once the ink was ready, it was put on a plastic syringe, which was then stored at 4 °C for 30 min to slow the geopolymeric reaction. Moreover, the syringe was placed in the 3D printer equipped with a pressurized vessel and an extruder. Subsequently, the inks were extruded through a capillary nozzle at room temperature, to produce layers of geopolymeric filaments that resulted in lattices. The structures will be characterized and tested on their ability to remove anionic contaminants from water.

Keywords: 3D printed geopolymers, Zeolites, Active carbon

ABS 591

CHARACTERIZATION OF TREATED GLASS SURFACE BY OPTO-MÉCHANICAL TECHNIQUES

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In the south of Algeria (Sahara), sand wind is responsible for the degradation of the surface of a large number of objects, especially brittle materials such as ceramics and glass. In the case of glass, the impacts induced by the sand particles on the surface can significantly reduce the breaking strength and light transmission by diffusion incident light diffusion. In this work we strengthened the glass by the reinforcement of its surface by thermo-chemical methods: ion exchange by chemical tempering and thin layer deposition by spray pyrolysis. For these two methods, there are many parameters involved, which must be controlled to have a good result. For the first method, we applied a chemical quenching treatment by diffusion of Potassium from a bath in the place of Sodium existing in the glass surface. The soda lime glass sample was submitted to this chemical treatment in order to introduce compressive stresses in the surface. The second treatment results in the spraying of a solution of a finely atomized Zinc metal salt with a carrier gas (compressed air) on the heated substrate on the surface of which the precursors react to form a film. The drops of the aerosol are directly projected on the substrate, the solvent evaporates and the decomposition of the precursor takes place to give the product layer. Several techniques were used to evaluate the influence of the time and temperature of the ion-exchange and of the spray-pyrolysis parameters on the surface characteristics of thereinforced glasses and compare these two reinforcement techniques; such as Vickers indentation, solid particle erosion test, 4-point bending test, and spectroscopy.

Keywords: Strengthened glass, ion exchange, spray pyrolysis

ABS 586

TOWARDS A CIRCULAR ECONOMY IN THE CERAMIC TILE INDUSTRY - CONSIDERING THE RAW MATERIALS ORIGIN AND TRANSPORTATION MODE IN NOVEL MATERIALS DESIGN

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A critical issue in the ceramic industry is raw materials transportation. European Union (EU) policies are mainly concerned with environmental problems related to the exponential increase of waste. In this context, new EU directives promote waste prevention and recycling through clean technologies and residue management. These directives, together with high disposal costs, currently motivate the ceramic industry to seek recycling solutions of ceramic waste both in the same production system as well as in different ones. Although the economic/environmental impact of transportation mode and distance is potentially high, this issue is less addressed. In order to fulfil this gap, this study deals with designing increasingly more “green” porcelain stoneware tile formulations by including consequently higher amounts of short-distance raw materials. Samples were obtained by standard powder processing routes and sintering conditions (1200 °C, 45 min). Technological properties and microstructure of the ceramic bodies were investigated using various analysis techniques such as X-ray Powder diffraction (XRPD) and Scanning Electron Microscopy. It will be shown that technologically valid products with lower environmental impact can be obtained by considering transportation emissions.

Keywords: Porcelain stoneware, materials design, environmental impact

ABS 560

USE OF ANODIZING SLUDGE TO CONTROL THE POROSITY OF GEOPOLYMER FOAMS

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The coalescence phenomenon is the Achilles heel in the production of porous geopolymers by the direct foaming technique, since the control the pore size distribution becomes a difficult task. In most of the published studies, this problem is solved through the addition of chemical stabilizing agents, such as surfactants.

In this study, a waste resulting from the surface aluminium treatment, the Al-anodising sludge, was used, as a stabilizing agent, in the production of porous geopolymers by the direct foaming technique. The effect of the Al-anodising particle size distribution and of the aluminium powder amount in the porous architecture of the synthesized materials was studied.

The developed porous geopolymers were characterized in terms of apparent density (kg/m3), total porosity (%) thermal conductivity (mW/mK), moisture buffering capacity (MBV), compressive strength (N/mm2) and setting time (min).

It was observed that the addition of Al-anodising sludge to the geopolymeric metakaolin-based paste allowed controlling the morphology and pore size distribution. It was possible to produce porous geopolymers with a porous architecture suitable for tailored applications. For example, lightweight materials (~ 290 kg/m3), thermal insulating materials (~ 79 mW/mK) or materials with high hygroscopic control.

Keywords: Geopolymer foam, Control porosity, Anodizing sludge

ABS 549

FREEZE-CASTING TECHNIQUE TO FABRICATE CEMENT PASTE STRUCTURES WITH ORIENTED POROSITY

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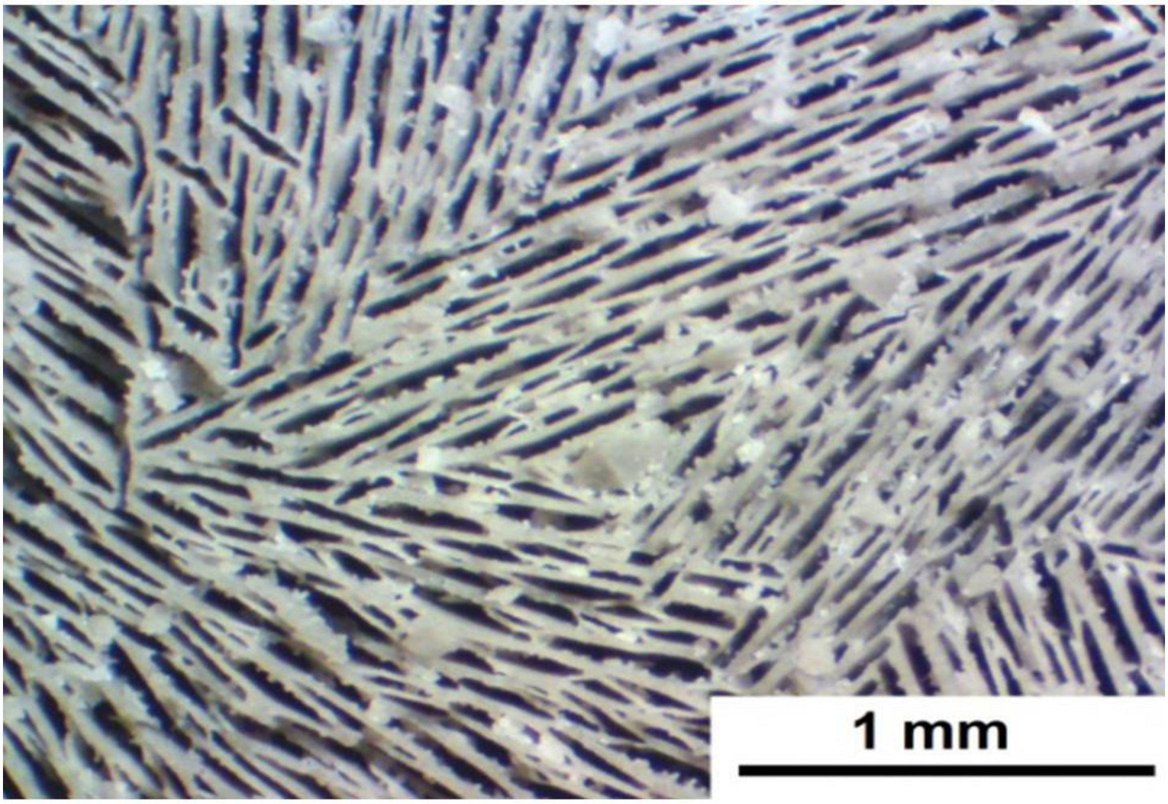
Portland cement has been a material used in civil construction since its discovery until today, its characteristics and properties are already well known, widespread and used all over the planet. New ordered porous materials can favor the emergence of advanced applications for the cement, such as lightweight mortar, thermal or acoustic insulation, some specific types of filters that can separate phases and perform desalination of water, as well as fabrication of permeable pavements. The fabrication methods of porous ceramics are greatly responsible of the material structure and its properties. Among them, the freeze-casting technique is a process leading to anisotropic ceramic structure with oriented pores. Indeed, this process enables the orientation of the porosity by freezing a ceramic suspension with a certain concentration of solid particles diluted in an aqueous or organic solvent. During the solidification step, the solvent transforms in crystals, ordering the solid particles in the direction of the temperature gradient. After sublimation of the mixture solvent, the porous structure results in the replica of the frozen suspension. In this context, suspensions with several proportions of cement, water and dispersant, were studied to find the adequate proportions to perform correctly the freeze-casting method. Samples were then solidified without orientation and using a domestic freezer or liquid nitrogen, before the sublimation and hydration steps of the cimenticious materials. The specimens were characterized by optical microscopy, x-ray microtomography, measurements of density and porosity, and compressive test. The results show that the orientation process applied to the cement was a success and demonstrated an increase in the compressive strength of the hydrated samples oriented with liquid nitrogen, as well as an increase in the open porosity of the structure.

Keywords: Portland cement, Freeze-casting, Macroporous structure



ABS 521

INVESTIGATION OF PYROPLASTIC DEFORMATION OF BONE CHINA REFORMULATED WITH Na AND K-FELDSPAR ADDITIVES

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Bone china has superior properties such as translucency, high strength and exceptional whiteness when compared to other types of whitewares. However, it is difficult to produce bone china because of its high pyroplastic deformation i.e., permanent distortion of its shape during sintering between 1200-1250°C. Pyroplastic deformation is mainly due to the effect of glassy phase which develops during firing in the ceramic body, causing the product to deform under its own weight because of gravity. Therefore, the deformation tendency is related to mainly viscosity of glassy phase and hence firing cycle. In this study, since the viscosity of glassy phase depends on its composition, the reformulated bodies with varying amounts of either individual or mixtures of sodium and potassium feldspars were formulated to control the viscosity of the glassy phase formed in bone china body. The effect of sodium and potassium feldspars on pyroplastic deformation behaviour of bone china was investigated. For this purpose, bone china bodies were prepared using bone ash, sodium-potassium feldspar and kaolin. Thirteen different compositions were formulated by varying the amounts of feldspars and kaolin and keeping the amount of bone ash fixed. The prepared bodies were sintered for 2 hours at a rate of 3°C/min at 1200, 1225 and 1250°C. To determine the pyroplastic deformation tendency, the rectangular prism–shaped test specimens were rested on a support by their two ends to allow them to move freely during sintering. The viscosity of glassy phase was calculated with the help of a mathematical model that takes into account that of calculated deformation index values. In addition, the sintered specimens were also characterised by measuring bulk density and water absorption values. Phase analysis was conducted using X-ray diffraction and the microstructure was studied with SEM. The analysis of X-ray diffraction for all the sintered samples confirmed mainly the presence of beta-TCP and anorthite crystalline phases. As a result, it was observed that the bone china body reformulated by using only the sodium feldspar as a flux provided the best results in terms of obtaining minimum amounts of pyroplastic deformation with zero water absorption and high bulk density.

Keywords: Bone china, Pyroplasticity, Fluxes

ABS 520

THE EFFECT OF Na_2O/K_2O MOLAR RATIO ON SELECTED PARAMETERS OF GLASS-CERAMIC GLAZES IN PRESENCE OF CaO AND MgO

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The most popular alkali oxides in ceramic industry are sodium and potassium oxides. Due to their different behavior during heat treatment, it is worth to know their influence on properties of ceramic glazes. This paper presents the results of research on glass-ceramic glazes from SiO2-Al2O3-CaO-MgO system with different Na2O/K2O molar ratio with an emphasis on the sintering process. Analysis of the sintering process allows for the appropriate design of the sintering curves in order to obtain a material with a high degree of crystallization. Both, chemical composition and heat treatment determine the final phase composition, which results in the functional properties of these materials.

Keywords: Glass-ceramic glaze, Molar ratio, Sintering

ABS 764

USE OF NEPHELINE SYENITE AS A FLUXING AGENT ON THE SINTERING BEHAVIOR OF THICK PORCELAIN STONEWARE FORMULATIONS

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Porcelain tiles are products with high technical characteristics. Especially its features excellent properties such as low water absorption, high breaking strength and frost resistance. These properties make them possible to be employed in different public areas. In ceramic tile production, different technological and product developments have occurred recently. One of the recent developments and applications in the field is the porcelain tiles with a thickness of 20mm and even higher, which is ideal outdoor pavings. Because of the increase in product thickness, the porcelain tiles with different designs and very high breaking strengths are obtained. However, due to the increased in thickness, some productions problems are expected. Firstly, longer sintering times increase the cost. Some mechanical problems may also appear during cooling. Furthermore, dense black core and some deformation problems can be observed.

In this study, the use of nepheline syenite from local source (Buzlukdag area, Kirsehir, Turkey) as a fluxing agent in thick porcelain tiles formulations, with particular attention to its effect on sintering behavior, were investigated. The raw material represents one of the largest and unaltered alkaline intrusive body in Central Anatolia region of Turkey. It's effect on the rheological behavior and the technical properties of the representative bodies were also detailed.
The results showed that the nepheline syenite are very suitable for the sintering of thick porcelain tiles with the required technological properties.

Keywords: nepheline syenite, ceramic

ABS 516

SILVER DOPED GEOPOLYMER AND ITS DISSOLUTION BEHAVIOUR

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Geoploymers are produced by alkali activation of aluminosilicates such as metakaolin, fly ash and slug etc. Alkali ions provide the charge balance associated with the AlO4- tetrahedral unit. It is known that alkali ion can be exchanged by other ions apart from alkali ions such as NH4+, Ca2+, Ba2+, Sr2+, Pb+, Ag+ etc. By using this ion exchange property of the geopolymers, various materials can be synthesised such as mullite, anorthite, celsian, etc. upon calcination. This study aims to develop an antibacterial material. For this, metakaolin based geopolymer was doped with silver by ion exchange process. The doped geopolymer was calcined at different temperatures up to 1050 oC. Release of silver ions from the calcined samples into water was determined by atomic absorption spectroscopy. The effect of calcination temperature on the phase development of the exchanged geopolymer and on the release of silver ion into water will be reported.

Keywords: Geopolymer, Silver ion exchange, Antibacterial

ABS 470

PROPERTIES OF RAW GLAZES CONTAINING DOLOMITE AND WOLLASTONITE

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Raw glazes are still often preferred to frits because the desired properties can be achieved at a lower cost in processes utilizing a peak temperature >1200 °C. Energy savings by lowering the peak temperature or shortened firing cycles require adjustments in the glaze composition towards better and faster fusibility. The chemical durability of the resulted glaze surfaces is important for hygienic and aesthetic properties.

The influence of wollastonite and dolomite on properties of raw glazes was studied. The amount of CaO and MgO in the compositions was chosen within a wide range to ensure glazes ranging from glossy to mat appearance. The melting behaviour was observed by hot-stage microscopy. The glazes were also fired industrially both in a fast-fired gas kiln for floor tiles (50 min) and in a traditional gas kiln for sanitaryware (25 hours). The gloss of the fired surfaces was measured with a reflectometer. The durability of fast-fired glazes in hydrochloric acid, citric acid and potassium hydroxide was studied with several different methods. The appearance of the corroded glazes was classified according to a standardised visual method, ISO 15454-13, and was complemented with more refined methods. Morphological and chemical composition were studied by SEM/EDXA. The crystalline phases in the glazes were identified by XRD. Surface topography was examined by a non-contact optical profiler. The concentration of dissolved ions in the acid solution after the corrosion test was analysed by ICPS.

Melting behaviour and surface structure on the raw glazes containing wollastonite and dolomite as raw materials depended both on the total content and the ratio of CaO and MgO in the glaze. Low content of alkaline earths gave incomplete fusion, while higher content improved the melting behaviour. Main crystalline phases found was wollastonite and diopside. The standard test could only find the most corroded surfaces and for more detailed studies these other methods must be used. Wollastonite crystals on the surface were corroded in the acidic solutions while in the basic solution small amount of silica was leached out.

The results can be applied to design the wollastonite and dolomite content in raw glazes to ensure a proper fusibility and desired surface structure and properties.

Keywords: glaze, melting behavior, durability

ABS 461

CRYSTALLIZATION IN FOAMED GLASSES

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Foamed glass is a lightweight material used for thermal and acoustic insulation applications in construction and industry. It exhibits several advantages in comparison to insulation materials such as organic foams and mineral wool, e.g., water and steam resistance, freeze-thaw cycle tolerance, excellent chemical and thermal stability, and superior mechanical properties. In the last decade, the possibility of recycling different glass cullets and glassy waste materials into this high value added product has been demonstrated. In this contribution, we present the results of our investigation of the occurrence of crystallization as well as its influence on the foaming process and properties of the products.

Foamed glass can be prepared from a pristine glass or from a cullet. Preparation directly from cullet is more sustainable; however, the properties of thus prepared foamed glasses are usually inferior. One reason for this is related to devitrification process. Since crystals have a higher thermal conductivity than their amorphous counterparts, the thermal conductivity of the solid phase increases with crystallinity. Measurements on dense glass samples revealed that thermal conductivity increases by 1/3 even at moderate crystalline content. On the other hand, thermal conductivity can also be decreased by suitable modification of the glass composition. Preparation of foamed glass from pristine glass enables tuning of the composition to avoid crystallization. On the contrary, direct foaming of a cullet requires adaptation of the foaming mechanism or other corrective measures to hinder crystallization. The influence of glass composition, foaming additives and atmosphere on the crystallization will be discussed.

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Keywords: foamed glass, crystallization, synthesis

ABS 452

POTENTIAL OF SEVERAL WASTES SUCH AS BLAST FURNACE AND LADLE SLAGS FOR THE FORMULATION OF ALKALI ACTIVATED COMPOSITIONS

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Slags coming from metallurgical industries in Slovenia, e.i. electric arc furnace steel slag (EAF) and ladle furnace basic slag (LF), were characterized to evaluate their suitability to obtain alkali activated materials. To evaluate the reactive fraction of slags, a basic attack was performed [1]. Al and Si contents in the leachate were quantified by ICP/OES and ICP/MS. Using these values, the reactive Si/Al mass ratio can be calculated. Other metals were analyzed to understand the stability of the slags in alkaline environment: As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn. From the reactivity test results appears evident that slag A has higher reactivity with respect to slag R in alkaline environment. For both the slags the silicon content is higher with respect to aluminum content in the solutions. Heavy metals and amphoteric elements such as Sb, V, As and Mo are only slightly released. XRD diffraction on slag before and after alkaline attack was performed to evaluate both amorphous/crystalline nature of slag and the modifications induced by the alkaline environment. The nature of the slags is mainly crystalline and the main crystalline phases identified are Q-quartz ($SiO2$), C-calcite ($CaCO3$) and P-portlandite ($Ca(OH)2$), with a decrease of quartz and calcite and an increase of portlandite after the basic attack. Quartz reacted mainly in slag A dissolving in the solution while slag R shows lower reactivity of silica. To evaluate the hazardousness of the slag, leaching test in distilled water for 24 h was performed according to European norm EN 12457. Solid residue was separated by filtration and eluate solution, after acidification (with $HNO3$ to pH = 2), was analysed by ICP/AES to determine the amount of heavy metals. From the results appears the not hazardous nature of both the slags. pH of slags was also measured at t = 0 and after 24 h resulting that one slag presents pH 10.2 and 10.3 and the other 11.6 and 11.3 respectively. The investigated slags are alkaline activated to obtain consolidated materials and the effect of ageing, curing and particle size on the mechanical properties were studied.

Acknowledgments
Project ERAMIN 2, Lightweight alkali activated composite foams based on secondary raw materials (FLOW), Project ID-94, 2017 ERA-MIN Joint Call; Coordinator: Dr Vilma Ducman, ZAG_Slovenia.

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Keywords: alkaline activation, slag, leaching test

ABS 404

MODE-I FRACTURE TESTING OF ALKALI ACTIVATED MATERIALS

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Objective In an attempt to reduce the CO2 emissions related to the production of cement and ceramic materials, a new class of materials known as alkali activated materials (AAMs) has rapidly grown in interest in the last two decades. AAMs have been increasingly investigated as a result of an emerging process based on alkali activation of precursors able to consolidate at room or slightly higher temperatures. Thanks to polycondensation reactions between a solid aluminosilicate source and an alkali activator, a mainly amorphous 3D network of aluminosilicates with binding properties is formed. One of the main advantages of AAMs is the possibility of using waste-based powders thus promoting a circular economy approach. In this paper, three different coal fly ash-based alkali activated mortars are studied in order to investigate their fracture properties.

Materials & Methods Carbon fly-ash was used as precursor. Three different mixes were obtained by changing the type of aggregate (i.e. silica sand with two different maximum size or expanded perlite) which functioned as the dispersed phase.
Small-scale 70 mm × 70 mm × 300 mm notched beams were constructed together with additional prisms and cylinders for material characterization. The small-scale beams were loaded in a three-point bend setup to investigate the Mode-I fracture properties. A clip-on gauge was used to conduct the test in CMOD control. Digital image correlation (DIC) on the side face of the specimens was used to get an insight into the size of the fracture process zone and compare the load-point displacement with the values obtained from LVDT readings.

Results The load versus CMOD plots confirmed that the AAMs are quasi-brittle materials. The entire post peak softening curve was obtained. The load versus load-point displacement obtained from the average of two LVDTs compared well with the same curved obtained from DIC readings. However, DIC curves were typically stiffer than LVDT curves, which suggests that some initial compliance of the testing setup might influence the LVDT readings and therefore should be critically revised. The fracture energy was determined from the work of fracture and resulted highly dependent on the type of dispersed phase rather than on the size of the aggregate itself. The values of the fracture energy were consistent with those of similar cement-based mortars. DIC contour plots were employed to determine the size of the fracture process zone, which resulted relatively comparable with the fracture process zone of a portland cement mortar with similar aggregates.

Conclusions The Mode-I fracture properties of three AAMs were investigated by means of three-point bend tests of small-scale notched beams. The fracture energy depended on the type of aggregate employed and its values were consistent with those of similar cement-based mortars. Similarly, the size of the fracture process zone compared well with similar cement-based mortars.

Keywords: fracture testing, carbon fly-ash, fracture energy

ABS 377

PRIMARY RESEARCH ON PORCELAIN WASTE UTILISATION

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Due to low sinterability, hard porcelain waste is mainly used as an additive (up to 10% by weight) to the bodies for the production of sanitary wares. The increase of recyclability for this waste could result in economical and environmental benefits. In this primary study, sinterability was examined depending on the grain size distribution. Several sintering activators, such as ZnO, CaO and MgO was introduced into porcelain waste up to 10 wt%. In this work, influence on various technological parameters i.a. shrinkage, bulk density, flexural strength and water absorption were studied. Phase composition of obtained materials was studied by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) with EDS microanalysis. All of obtained samples showed significantly increased flexural strength comparing to samples made from unprocessed porcelain waste.

Keywords: porcelain waste, utilization

ABS 371

LOW COST SUPPLEMENTARY CEMENTITIOUS MATERIALS FOR NEW GENERATION COMPOSITE CEMENT

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Cement manufacture will be encounter to the drastic changes in near future. Despite the various benefit of using them, the low cost of new generation cement grabbed the attention to them. Ternary composite cements made of clinker, limestone and calcined clay present the high potential to be used as general-use cement with decrease associated CO2 emission and embodied energy. Also, it is assumed that the constructions which are going to use the composite cements are much more durable. Recently, there were several research about the usage of meta-kaolinite as SCM. But the high price of meta-kaolinite limits its use in concrete to premium application. In this study the potential reactivity of schist type material as mine overburden were evaluated. The virgin schist (MV) and by 15% additive of limestone (ML) were heat treated to substitute the OPC. The obtained results were compared to the meta-kaolinite as benchmark.

The overburden materials were received from mine inside Turkey. The Kaolinite is provided from one of the known sources in Istanbul. The virgin materials were analyzed for phase distribution by the different characterization method. The Ordinary Portland Cement (OPC) is an ENS 197-1 CEM 42.5 R type I which is provided by AkcanSA Cement Manufacture Company. Both virgin schist (MV) and with 15% limestone additive (ML) were considered to be used as cement substitution in proper ratio. To evaluate the materials, several types of analyses have been performed. First, the potential reactivity of both un-treatd powders were analyzed by the thermo-gravimetric method to identify the optimum decomposition temperature. Then, the phase analysis were done by means of X-ray diffractometer (XRD) while the scanning electron microscopy (SEM) photos elaborate phases present in the raw material. The materials were calcined to the determined temperature range and used as 30% of cement substitute in calcined schist cement paste samples for the best indicator which is compressive strength test. MV, ML and meat-kaolinite samples were evaluated by compression strength test through the 2, 7, 28, 50 and 90 days of setting time.

Results represent the acceptable compressive strength of limestone calcined schist cement sample comparing to the calcined virgin schist cement and meta-kaolinite. The compressive strength of ML shows the unexpected resemblance to ordinary Portland cement paste.

According to this study, it was concluded that the substitution of cement with mine overburden schist type materials is beneficial.

Keywords: Calcined Schist Cement, Limestone, Mine Overburden

ABS 370

UNDERSTANDING EXPANSION IN LWA PRODUCTION: THE ROLE OF THE GLASSY PHASE

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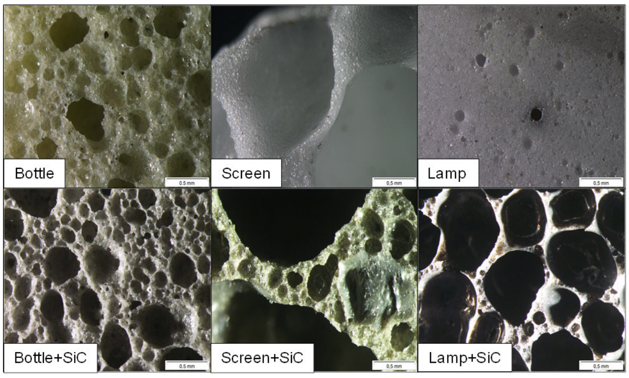
Ceramic foams represent highly valuable materials for civil applications, given their low bulk density, thermal and acoustic conductivity, especially in the view of almost zero-consumption buildings. Furthermore, their high thermal and chemical stability turn them a valid alternative to polymeric foams. Glass-based foams can be successfully used to produce lightweight aggregates at lower firing temperatures, starting from glass wastes, thus reducing costs and environmental impact. However, a clear relationship between the glass properties and the final porous structure achieved is missing. It is of paramount importance to keep bloating and pores morphology under control to govern the mechanical and thermal performance of foams. Thus, the focus of this work is to predict the technological behavior of glass (alone and after the addition of SiC as high temperature foaming agent) in order to tailor batch formulation and process conditions to have well defined material bulk properties. For this purpose, glass scraps derived from different industrial processes (bottle, lamp, screen) were selected. They were characterized for the relevant properties affecting the expansion during heating: chemical and phase composition (XRF and XRD, respectively) as well as density, shear viscosity and surface tension at high temperature (estimated by predictive models based on the glass chemical composition). A set of experiments was carried out (in electric kiln and hot-stage microscopy) to study the effect of processing conditions (firing temperature, heating rate, specimen size) on bloating phenomena occurring during heating. The parameters considered are: degree of expansion, characteristic temperatures of sintering, expansion and collapse, bloating rate, foam microstructure (size and shape of pores and septa). Furthermore, the effect of chemical and physical properties on SiC decomposition was examined. Comparing samples with the same shear viscosity a different effect on the microstructures evolution was observed. This phenomena was emphaticized by the addition of the expanding agent, leading to the formation of foams with strongly different characteristic parameters. The goal is to enable a mix design approach to get the desired properties of glass foams based on the chemical and physical characteristics of starting glass wastes.

Keywords: ceramic foam, glassy phase, lightweight aggregates



Effect of chemical composition and SiC addition on microstructur definition

ABS 327

EXTREMELY LIGHT AND LOW THERMAL CONDUCTIVITY CORK-GEOPOLYMER COMPOSITES: A SUSTAINABLE MATERIAL TO ENHANCE BUILDINGS' ENERGY PERFORMANCE

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In 2015, the United Nations member states adopted the "2030 Agenda for Sustainable Development" in which 17 development goals were proposed. Among them, climate change and affordable and clean energy in particular require urgent action. One way to tackle climate change is by greatly reducing the current, and unprecedented, CO2 emission levels. In this regard, buildings may play a vital role, considering that they are responsible for 36% of the total carbon dioxide emissions in the EU. One approach to decreasing the carbon footprint of buildings is by reducing their energy consumption, the main source of greenhouse gas emissions, and for that reason the development of ultra-light, environmentally friendly, sustainable, low cost and low thermal conductivity materials is imperative. In this study, and for the first time, cork was used as a low density aggregate in the production of ultra-light-weight and low thermal conductivity geopolymer composites. Cork is a uniquely sustainable material, and the geopolymers themselves were aluminosilicates derived from the valorisation of industrial wastes. Besides their extremely low density (260 kg/m3) and low thermal conductivity (~70 mW/m K), which are amongst the lowest values ever reported for geopolymers, this sustainable composite is thermally stable up to 200 °C, does not release any toxic fumes when exposed to fire, and also shows interesting acoustic insulation properties, these being crucial advantages over polymeric based foams such as expanded polystyrene (EPS) and extruded polystyrene (XPS).

Keywords: geopolymer, lightweight aggregate, composites

ABS 305

SHAPING TECHNIQUES OF POROUS ALKALI BONDED CERAMICS FOR ADSORPTION APPLICATIONS

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Alkali bonded ceramics (ABC) are synthetic and amorphous alkali aluminosilicates, also known as geopolymers, with properties varying among those of ceramics, cements, zeolites or refractories.

The microstructure is intrinsically mesoporous and several forming techniques can be exploited to modify the porosity from the micro- to the ultra-macro scale, creating hierarchical pore systems. Ice-templating allows, for example, to obtain ABC with mainly unidirectional anisotropic macro-pores, where the ice crystals act as pore network template, forming unique lamellar morphology. Microporous fillers, as zeolite, improve the porosity functionalizing the material for CO2 sorption applications.

Adsorbents in form of beads and spheres have lately received attention thanks to the good mobility, high packing density, ease of separation and reuse after regeneration. For this reason, several "spherification" processes are applied to obtain millimeter-size porous ABC beads, different in term of porosity and adsorption properties.

Indeed an injection-solidification method in different media, i.e. polyethylene glycol or liquid nitrogen, is exploited to produce different ABC beads. In addition, ABC beads are obtained by ionotropic gelation.

The process parameters are deeply investigated and the most performing samples are characterized in terms of morphology, macro- and microstructure, composition, porosity distribution and specific surface area together with the adsorption properties towards gaseous CO2 or dyes.

Keywords: Geopolymers, Shaping techniques, Adsorption

ABS 300

THE INFLUENCE OF THE AMOUNT OF ZIRCONIUM OXIDE ADDED, ON SELECTED THERMAL PARAMETERS OF GLAZES FROM THE SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O SYSTEM, WITH A VARIABLE MOLAR RATIO OF ALKALI OXIDES (Na_2O/K_2O)

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Glazes belong to the group of glass-ceramic materials. Due to the presence of amorphous and crystalline phase in glazes, theoretical analysis of these materials is complicated, because of interactions between the components in this system. Thermal analysis methods of physical phenomena and chemical reactions, in complicated systems, are helpful to understand the changes in glazes during the firing process.

In this paper, the glass-ceramic materials from SiO2-Al2O3-Na2O/K2O-CaO-MgO system were examined. The glazes were characterized by the constant molar ratio of SiO2/Al2O3 = 7 and CaO/MgO=1, but the molar ratio of alkali oxides was changed (Na2O/K2O=3.64; 0.97; 0.5). The zirconium oxide was added to this glazes in five different amounts (1.5; 3; 6; 12; 24 wt.%). In addition, the sample without zirconium oxide as the reference sample was prepared. To determine the effect of zirconium oxide on the thermal parameters the characteristic temperatures were measured, by using hot stage microscopy (HSM-Misura) and mechanical dilatometry (DL-Netsch). Based on this results the viscosity curves were designated. Furthermore for the description of the phenomena which occurs during the heating-cooling cycle Differential Scanning Calorimetry (DSC) was used. This data were linked with the results from X-ray fluorescence (XRF), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) with microanalyzer (EDS). All of the obtained results create a lot of interesting dependences, e.g. sodium and potassium oxide have different acting in glazes.

Acknowledgments

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Keywords: zirconium oxide, viscosity, DSC

ABS 287

DEVELOPMENT OF AN INNOVATE FIRE RESISTANT GEOPOLYMER BINDER

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In a context of circular economy, the valorization of by-products resulting from an exploitation activity is a growing concern for the industrial. The National Agency for the Management of Radioactive Waste (Andra) is carried out work for the construction of a geological disposal center for radioactive waste. If its construction is allowed, its progressive operation should generate the excavation of several million tons of rock. This rock is mainly composed of clay minerals, carbonates and tectosilicates. Among the opportunities for the valorization of this clay, the development of new fire resistant and durable construction materials which can be used in the storage site, appear as promising candidates. These geopolymers materials have garnered increasing interest over the last decades because of their high working performances, wide range of applications and low environmental impact. Thus, this study, supported by Andra under the "Investments for the Future Program, aims to formulate thermally resistant geopolymer composition.

To achieve this objective, different raw materials and mix calcined with different processes and temperatures (flash and furnace calcinations) were used. Different alkaline silicate sources were also used for geopolymer synthesis. The obtained materials were subjected to a heat treatment at 1000 °C. In order to evaluate their thermal resistance, the mechanical properties and the mineralogical composition of the samples before and after heat treatment were studied.

The thermal resistance tests demonstrated the possibility to formulate thermal resistant geopolymer samples. The results show that geopolymer materials exhibit good mechanical resistance, which depend on the type of raw material. It was also demonstrated that the use of several clay allows the in-situ formation of zeolitic phases and wollastonite, which plays the role of reinforcement at high temperature.

Consequently, geopolymer could be a promising candidate to application, which requires the good thermal resistant properties.

Keywords: Geopolymers, Raw materials, Thermal resistance

ABS 273

COMPRESSIVE PROCESSING OF CLAY RESIDUE-BASED GEOPOLYMERS: INFLUENCE OF THE Na_2SiO_3/NaOH RATIOS ON COMPRESSIVE STRENGTH AND MICROSTRUCTURE

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Geopolymers were synthesized from clay residue with the compositions of muscovite, mica, kaolin, sanidine, and quartz phases. Moreover, we will replace a common casting by a new method which is pressing. The pressing method can be enhanced the strength of geopolymers. Firstly, clay residue was calcined at 700 °C in order to form the active starting materials, resulting in the higher dissolved in an alkaline activator solution. Calcined clay residue was mixed with the low amount of alkali activator solution at liquid/solid ratio of 2.25. Homogeneous semidry powder was formed by using hydraulic pressing machine at 20 MPa in order to produce geopolymers. In the present work, the influence of the Na2SiO3/NaOH ratios on compressive strength and microstructure of clay residue-based geopolymers was studied. The variable parameters for synthesis were the Na2SiO3/NaOH ratios in the rage of 0.44-3.43. After geopolymerization, the geopolymer samples were evaluated in mechanical properties and microstructure. The highest compressive strength was equal to 27 MPa. With increasing the ratios up to 2.25, the compressive strength of geopolymers increased but the strength decreased when the ratio was 3.43. FT-IR results showed that adsorption band at 1010-1015 cm-1 presented the asymmetric stretching vibrations of Si-O-Si and Si-O-Al bonds of the geopolymer network and then shifted toward the lower frequency. XRD results showed an increase in amorphous phase and the decreasing intensities of disordered muscovite mica and sanidine phases in geopolymers. These were explained to be due that samples contained more geopolymeric gel for occurrence of denser microstructure in an increment of these ratios, showing dense pores volume as decreased with an increase in the Na2SiO3/NaOH ratios.

Keywords: Compressive processing, Compressive strength, Geopolymers

ABS 262

UPCYCLING OF CONDITIONED MSWI BOTTOM ASH INTO POROUS CERAMICS BY MEANS OF STRONG OR WEAK ALKALI ACTIVATION

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This study reports an integrated approach to valorise vitrified municipal solid waste incineration (MSWI) bottom ash into highly porous and strong materials. After the extraction of ferrous and non-ferrous metals from MSWI bottom ash, the residue was smelted by means of an electric arc furnace and quenched in water, thus obtaining a chemically stable CaO-Al2O3-SiO2 glass. The glass was further subjected to two different processes, based on alkali activation, to produce foams. In the first one, the vitrified bottom ash was mostly dissolved in a strong alkaline solution and transformed into a porous inorganic polymer by addition of metallic aluminium powder followed by curing at 60 °C. In the second approach, the glass was partially dissolved in a much weaker alkaline solution. After the formation of gels on the surface of the glass, the “gelified” suspension was foamed by intensive mechanical stirring with the support of a surfactant and dried at 40 °C. The dried foam was finally fired at 1000 °C, thus obtaining a porous glass-ceramic. Both strategies yield strong porous ceramics that could be potentially applied as thermal and acoustic insulators in buildings.

Acknowledgement
This project has received funding from the European Union’s EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No 721185.

Keywords: Porous ceramics, Alkali activation, Waste-derived materials

ABS 261

RESIDUAL STRESSES IN CERAMIC SLABS: INDIRECT EVALUATION AND PREVENTION

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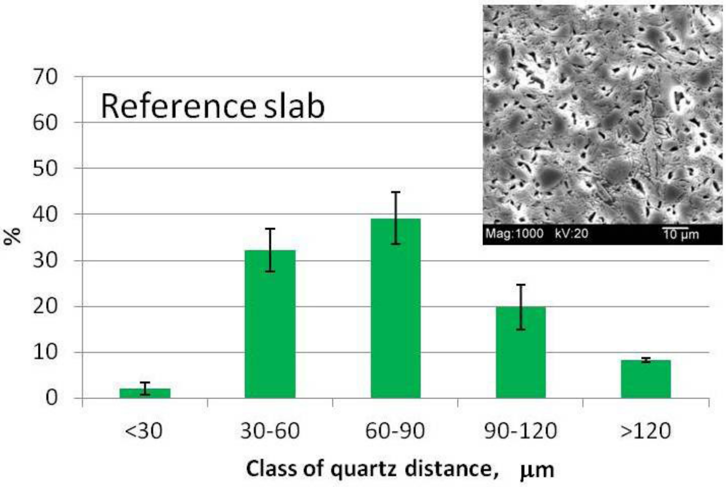
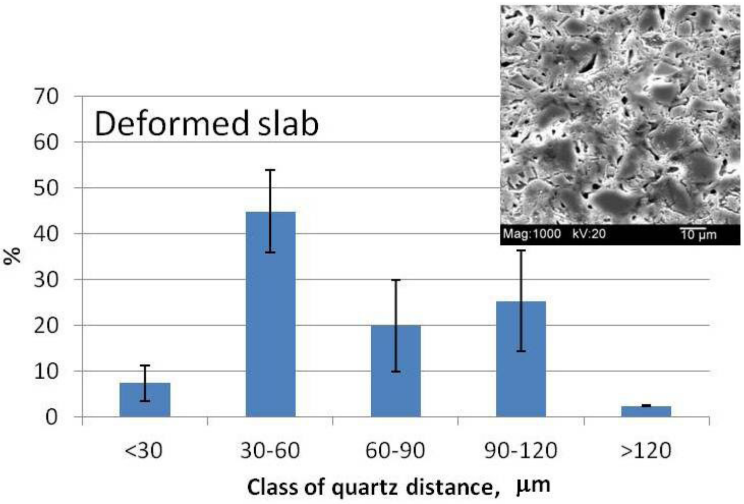
In the last years, porcelain stoneware tiles have been object of a rapid evolution and, nowadays, it is possible to produce high quality tiles with very fast firing cycles and in several sizes, from the traditional 30x60 cm till the largest format 480x180 cm. The phenomenon of post-firing deformations, due to the residual stresses occurring in non-equilibrium firing conditions, is rather well known especially for the largest slabs.
To date, a method to quantitatively determine residual stresses in a ceramic slab is not available and only its effects are visible. The present work aims to provide a series of quantitative measures useful for estimating the risk of occurrence of residual stress in the ceramic slabs, that can give rise to post-firing deformation phenomena. A series of quantitative analyses were carried out on two fired porcelain stoneware slabs, one with a visible post-firing deformation and the other one free of deformation (reference). All the analyses were aimed to evaluate and possibly to quantify the microstructural heterogeneity that could cause residual stresses. In particular, by considering three specimens taken from different positions of each ceramic slab, the following characteristics were determined:
1) degree of raw materials mixing through the distribution of distances between quartz grains;
2) degree of powders compaction through the dimensional distribution of closed pores;
3) degree of firing through the composition of the amorphous phase and its representation on ternary diagrams (RO2, R2O3, R2O + RO).
Results showed that the degree of compaction and the degree of firing of the slab with a post-firing deformation and the reference slab free of deformation were rather similar. On the other hand, respect to the reference slab the analyzed specimens of the post-firing deformed slab showed significant differences in terms of distribution of quartz grain distances. In particular, the bi-modal distribution of the quartz grain distances clearly indicates a not optimized raw materials mixing in the post-firing deformed slab (Fig.1).





The results (the distribution of quartz grains distances, the ternary diagrams representative of the composition of the amorphous phase and the distribution of the pore sizes) relative to different positions of the ceramic slab are able to highlight those heterogeneities that can create / favor critical levels of residual stresses. Therefore, the quantitative determinations proposed in this work represent an indirect evaluation of the risk of the occurrence of those residual stresses which, especially in large slabs, can give rise to post-firing deformation phenomena.

Keywords: Ceramic Slab, Residual Stress, Microstructure

ABS 241

DEVELOPING ALTERNATIVE GEOMATERIALS USING LATERITES FROM CAMEROON: REACTIVITY AND MECHANICAL PROPERTIES

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Lateritic soils are formed from alteration of kaolinite through the lixiviation process involving iron-rich mineral phases in which a high proportion of aluminium is replaced by iron, resulting in lower crystallinity of the related kaolinite, that induces low energy for their thermal activation making them suitable for the synthesis of geomaterials. In this work, we aim at using widely available lateritic raw materials in Cameroon, in order to prepare alternative binders or geomaterials for building purpose. In this scope, we have previously selected two raw laterites and optimized their thermal activation namely at 600°C. Regarding the understanding of the relation between the reactivity and the properties of use of these laterite-based geomaterials, we have investigated their behaviour under alkaline and acidic solutions. Both calcined laterites noted LAI and LAC were mixed with an alkaline solution (silicate modulus of 1.35) and acidic solutions (10 M of phosphoric acid or fulvic acid solution at pH2) for the design of geomaterials. The synthesized products were maintained at room temperature (20°C) and at 40°C for 7 and 28 days. The starting materials and the as-obtained geomaterials were subjected to structure and microstructure analyses as well as to physical and chemical characterizations. The physicochemical properties and microstructure characteristics were correlated with the mechanical properties using compressive test. The results showed that the dry compressive strength of each series of geomaterials increases with ageing time and temperature. The best mechanical performance was obtained when using 10 M of phosphoric acid solution, 48 and 59 ± 1 MPa for LAC and LAI respectively. It appeared that a higher iron content within the laterite may contribute to improve the strength under acidic condition (LAI (59 MPa) > LAC (48 MPa)) conversely to the behaviour obtained under alkaline medium (LAI (8 MPa) < LAC (27 MPa)). This trend is in agreement with the chemical interactions between iron phases and the phosphoric acid leading to the formation of amorphous binding iron-phosphate phases (berlinite, evidenced through FTIR and XRD). Further investigations are being performed in order to assess the interest of such laterites geomaterials. Indeed, compared to a common metakaolin-based geomaterials the synthesized lateritic geomaterials from this study exhibited higher dry and wet mechanical properties. Since the thermal activation of these laterites is, lower than 700°C (used for metakaolin), their use will also lead to significant firing energy gain. Thus the laterites based geomaterials appear more sustainable, low cost and environmentally-friendly.~

Keywords: Laterite, Geomaterials, alkalmine and acid solution, mechanical properties

ABS 228

STUDY OF VARIOUS POROSITY RATIOS USING SODIUM AND POTASSIUM BASED ALKALI ACTIVATORS IN LEBANESE METAKAOLIN GEOPOLYMER MORTARS

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The present work aims to investigate the influence of adding a liquid activator on various alkaline solutions (Na and K) for a Lebanese metakaolin-based geopolymer. Geopolymers are alkali-activated materials that have been holding, for the past two decades, the attention of scientists worldwide [1]. They have demonstrated to be environmental friendly materials that emit less CO2 than Ordinary Portland Cement (OPC). Within the first part of this study, the metakaolin was produced from the calcination at temperature of 700 degrees of a Lebanese local source of kaolin. Accordingly, the SiO2/Al2O3 and (Na or K)2O/Al2O3 ratios were specifically formulated in order to obtain the optimum mix for our experimental set up; highlighting as well the alkaline activators (Na and K) used; where the SiO2/Na2O ratio is equal to the SiO2/K2O = 1.5 [2]. Once these steps were taken into consideration; the silica, alumina, alkali activator (either sodium or potassium based) and water were all brought to the mixture in order to obtain the required mortars. The liquid activator was added according to a specific range varying from 5 to 20 % mass substitution of the two used alkaline activators (Na and K). Once elaborated in the laboratory, the various samples produced (4x4x4 cm) are cured at 60 degrees for 24 hours and were later on well-preserved for aging in appropriate conditions until respective mechanical properties are tested at 3 and 28 days. Consequently; this work will significantly study the influence of the use of liquid activators on pores formation in the mortars produced. This will proofread how the liquid activators affect the microstructure and the mechanical properties of the geopolymers. The mortars obtained, gave an obvious alteration when comparing the potassium based activator with the most common activator solution that is made of NaOH pellets and Na2SiO3. Results showed a visible high influence of the alkali-(Na or K)OH activators on the microstructural properties (pores networks and microstructure) and mechanical properties of the mortars produced due to a variation of the amount of the reacted metakaolin.

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Keywords: Mortar Geopolymers, Pores Characteristics, Mechanical Properties

ABS 397

DETERMINATION OF THERMAL PROPERTIES OF CERAMIC TILES BY LASER FLASH TECNIQUE

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Ceramic tile industry consumes a lot of energy during firing stage. Therefore, the assessment of thermal properties when designing the ceramic composition can turn into a key tool in terms of sustainability and energy saving control

Traditionally, thermal conductivity of ceramic specimens has been measured using different techniques such as the protected hot plate or the heat flow meter due to the simplicity of these methods. However, as ceramic tiles present roughness and sometimes even curved surfaces, these techniques are not entirely optimal for obtaining reliable values because they require perfect contact between the equipment device and the sample surface.

This work presents an innovative method to measure thermal properties, i.e, thermal diffusivity, thermal conductivity and specific heat in several tile samples using the laser flash technique (LFA). This method allows to determine the thermal properties of samples with a rough or curved surface because the detector does not contact the sample surface. LFA calculates the thermal diffusivity of materials by emitting a short energy pulse that heats the bottom surface of the sample and measures the temperature change taking place on the opposite surface of the sample by means of an infrared detector. With the values of thermal diffusivity, thickness and density of the sample as well as the average rise time of the signal recorded by the detector, it is possible to calculate the thermal conductivity. The specific heat of solids is determined comparing the difference of the signal height of the sample relative with the signal height of a well-known reference material.

Results revealed that it is possible to measure the thermal properties of ceramic tiles with different composition with high reliability. Likewise, a microstructural characterization of all ceramic samples was carried out by scanning electron microscopy and heating microscope to better understand thermal properties. Thus, some correlations between ceramic composition, fired specimen microstructure and thermal properties were found.

Keywords: Thermal properties, ceramic tiles, flash laser technique

ABS 205

GLAZED CERAMIC TILES WITH IMPROVED UPEC CLASSIFICATION

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In the production of glazed porcelain floor tiles decorated with dark colours it is very difficult to reach the maximum UPEC classification for the U classification (“Ussure de la marche”: trampling wear). According to this norm the variation of the classes for glazed ceramic tiles varies in the same direction as the variation of PEI.

The abrasion resistance of glazed ceramic tiles is a complex property as it is influenced both by the rate of removal of the material and by the resulting aesthetic appearance after the wear test performed. The rate of removal of the material depends on the mechanical properties of the glazed coating, its microstructure and the residual porosity. The thickness of each layer used (engobe, glaze, topcoat), as well as its relative thickness, also influence the performance of the system, weakening or reinforcing the top layer. On the other hand, the aesthetic aspect also requires an adequate combination of brightness and colours, to avoid the easy visual appreciation of the damages caused to the surface.

The production of glazed ceramic tiles with high resistance to abrasion wear requires the presence of a high strength transparent top coating.

Using coatings of different composition, applied with different thicknesses and fired at different temperatures, it has been possible to study the relationship between the wear resistance of the tiles, their surface mechanical properties (hardness, toughness, and scratch resistance) and their microstructure.

Keywords: Glaze, wear

ABS 200

3D PRINTING OF GEOPOLYMERS: THE PATH TO INNOVATIVE CERAMIC COMPOSITES

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Geopolymers are inorganic materials generally obtained by the reaction of alumino-silicate powder in an alkaline solution. They can consolidate at low or even room temperatures and possess good mechanical properties, weather and heat resistance, which make them suitable for a wide range of applications, such as structural materials, thermal insulation, and so on.

Our group developed mixtures based on geopolymer for additive manufacturing of porous components via direct ink writing (DIW). We optimized the rheological properties in order to obtain suitable inks for the production of highly porous lattices. It should be noted that, as geopolymer mixtures are subjected to ongoing poly-condensation reactions, their viscosity changes with time in what can be seen as a 4D printing process. Different materials were added to the mixture, such as fibers and micro particles, to produce innovative 3D printed geopolymeric composites.

Keywords: Additive manufacturing, Geopolymer, Composite

ABS 190

VALORIZATION OF CLAY MATERIALS FROM CENTRAL AFRICAN REPUBLIC (CAR) AND PLANT SKINS WASTE AS SILICATE CERAMICS

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The present paper aimed at investigating the sintering behavior of some common clays readily available in Central African Republic (RCA) for their use as ceramic products (building purposes). Three deposits were identified close to Bangui (capital of RCA) and labeled as NZ1, NZ2 and KO. Preliminary trials were performed to select a common plant waste that can bring supplemental flux to promote the sintering of the related clay materials. The physical and chemical characterizations of the three clays were conducted together with mineralogical and thermal analyses. The sintering behavior was studied using disk of each clay sample obtained by unidirectional pressing. NZ1, NZ2 and KO are mainly constituted with kaolinite, illite, quartz, goethite and hematite as major phases. In addition, KO contains a significant amount of associated organic compounds and exhibit more than 80% of grains < 10 m that may contribute to the development of cracks during sintering. According to the thermodilatometry analysis of each clay, it appears that the densification begins at 1000°C, 1028°C and 1060°C for KO, NZ1 and NZ2 respectively. The final shrinkage noted at 1200°C was higher for KO (19%) than for NZ1 (10%) and NZ2 (3%). The thermal and mechanical properties obtained for the sintered samples indicate that the optimized sintering temperature for NZ1 is close to 1100°C, while NZ2 was not significantly densified and KO exhibited cracks development even after firing at 1000°C. Regarding the latter trends, 5 to 15 mass% of a dried powder of the selected plant skin waste was added to NZ1 and NZ2. In the case of KO, different amount of NZ2 was added in order to balance the high shrinkage and inhibit the crack development. The best mixture regarding the mechanical and thermal conductivity results was obtained when adding 5 mass% and 10 mass % of the plant waste to NZ1 and NZ2 respectively. Furthermore, when mixing 90 mass% of KO with 10 mass% of NZ2, the sintering behavior was improved at 1000°C. Indeed, the present work has contribute in clarifying the mineralogical and chemical compositions of three important clay deposits in Bangui (RCA) and their potential use for producing silicate ceramics for building purposes. Furthermore, the introduction of a plant waste as a flux source was helpful in optimizing the sintering of NZ1 and NZ2 and lowering the densification temperature, thus very promising for environmental and economic issues in RCA and in most tropical region countries. µ

Keywords: Clays, silicate ceramics, plant skins waste, sintering, properties of use

ABS 171

SINTERING OF YE'ELIMITE

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The production of Calcium Sulfoaluminate (CSA), Belite-Calcium Sulfoaluminate-Ferrite (BCSAF) or Alite-Calcium Sulfoaluminate (ACSA) clinkers involves lower embodied energy and CO2 emissions compared to the ordinary Portland cement (OPC), because they require less limestone, lower grinding energy and lower clinkering temperatures than OPC clinker [1]. Ye'elimite (Ca4Al6O16S or C4A3S'(*)) is the main phase in CSA clinkers and also a key component in BCSAF and ACSA clinkers [2,3]. Therefore, the detailed understanding of ye'elimite sintering may be the key for solving burnability(†) encountered in the production of CSA clinkers. The purpose of the current work is to investigate the ye'elimite formation mechanisms by solid-state reactions from pure raw materials: calcium carbonate (CC'), alumina (A) and gypsum (CS'H2). This study was conducted ex-situ using X-ray diffraction and scanning electron microscopy to get information about mineralogical and microstructural assemblage at different sintering temperatures. Ye'elimite forms on calcium aluminate grains. Its formation was accelerated by increasing sintering temperature and sintering time, also by decreasing the size of the alumina grains. Regrinding, re-pelletizing and refiring increases contacts and reactions between calcium aluminate phases and calcium sulfate phase, which implies the formation of ye'elimite with high purity.

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(*) The cement phase notations are used in this work (C= CaO, A = Al2O3, S' = SO3, C' = CO2, H = H2O).
(†) The burnability is the facility with which the components of CSA cements raw mixture are combined.

Keywords: Calcium Sulfoaluminate, ye elimite, Sintering

ABS 168

POWDER RHEOLOGY AND COMPACTION BEHAVIOR OF NOVEL DRY GRANULATES FOR CERAMIC TILES

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The current evolution toward the production of porcelain stoneware slabs with always increasing size and variable thickness determines the demand for performing and high-quality ceramic powders, especially in terms of rheological and compaction behavior. On the other hand, environmental and economic reasons row against the now dominating spray-drying process, because of its large water and energy consumption. However, spray-dried powders are characterized by spheroidal granules with unrivalled rheological and compaction properties [1, 2]. The alternative powder technology, based on the dry route, suffered from unsatisfactory flow properties, dictated by granule shape and stiffness, that reflected on uneven compaction and microstructural defects in the fired tiles. Nevertheless, such obsolete technology has been substituting by novel microgranulation processes, which provide rounded and soft granules by wetting-agglomeration-drying operations. Hence, dry granulates are claimed as a promising route for minimizing water and energy consumption while ensuring a good performance of the powders [3, 4]. Our goal is to test the dry granulates in the manufacture of porcelain stoneware tiles in comparison with spray-dried powders. For this purpose, industrially manufactured granulates were characterized for their rheological properties (grain size and moisture distribution, static and dynamic repose angles, poured and tapped density, mass flow, particles morphology) and compaction behavior (bulk density of green and dried bodies obtained with increasing applied load, green and dried modulus of rupture, microstructure of finished products). Results reveal that novel dry granulates have improved rheological and compaction properties, with respect to traditional dry granulates, and they approach the performance of spray dried powders. The still existing differences in the behavior of spray-dried and dry granulated powders are discussed in relation to microstructure and stiffness of granules.

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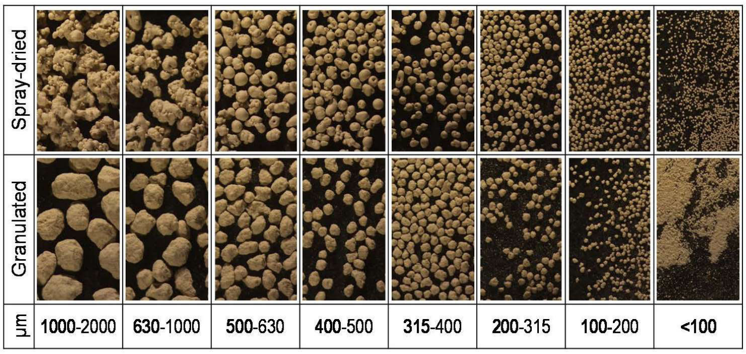
Keywords: Dry granulation, Porcelain stoneware, Rheological Properties



Comparison of particle size fractions: Microgranulated versus Spray-Dried bodies.

ABS 156

LOW-DENSITY GEOPOLYMER COMPOSITES THROUGH THE INCORPORATION OF EXPANDED POLYSTYRENE

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The study of alternative cementitious materials has been growing over the years. Alkali activated materials, also called geopolymers, are an economically viable alternative to replace Portland cement in some applications. Geopolymers are produced by the activation of materials rich in alumina and silica with alkaline solutions, Among the most used starting materials is metakaolin, since it exhibits a suitable reactive potential for the confection of geopolymers. This research investigated the production of a low density geopolymer composite, based on metakaolin through the incorporation of expanded polystyrene (EPS). The effects of volumetric amount (18, 35 and 53%) of EPS and diameter of the EPS beads (0.85, 2.16 and 6.00 mm) were evaluated. The composites obtained were subjected to mechanical strength tests, scanning electron microscopy, infrared spectroscopy and x-ray diffraction. Physical analysis of water absorption, apparent porosity and apparent density were also performed. All results showed the same trend in the charts. The strength of the composite reduced significantly from 47 MPa (0% EPS) to 9.62 MPa and 1.74 MPa, when using 53% EPS of smaller and larger beads, respectively.

Keywords: Lightweight geopolymer, Composite, Expanded polystyrene

ABS 134

DEVELOPMENT OF HIGH PERFORMANCE ANTISLIP COATING SUBSTITUTION TO GLAZE FOR CERAMIC TILES

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Ceramic tiles are one of the ceramic seb-sector with a high export/production ratio in the ceramic industry. Wall tiles, floor tiles and porcelain tiles are the main products of the ceramic tiles. Besides of the technical properties, antislip properties also be required for wet conditions. Antislip effect is generally provided by glaze layer containing different crystalline phases. Thefore this property is only provided by glaze layer. In this study, it is aimed to cover the glazed and unglazed tiles with a antislip polymer coating that cures in room conditions and provides antislip feature to the tiles.

Keywords: antislip, polymercoating, ceramic tiles

ABS 124

BIO-SINTERING OF AMORPHOUS SILICA BY HYDRO-PRESSURE DENSIFICATION

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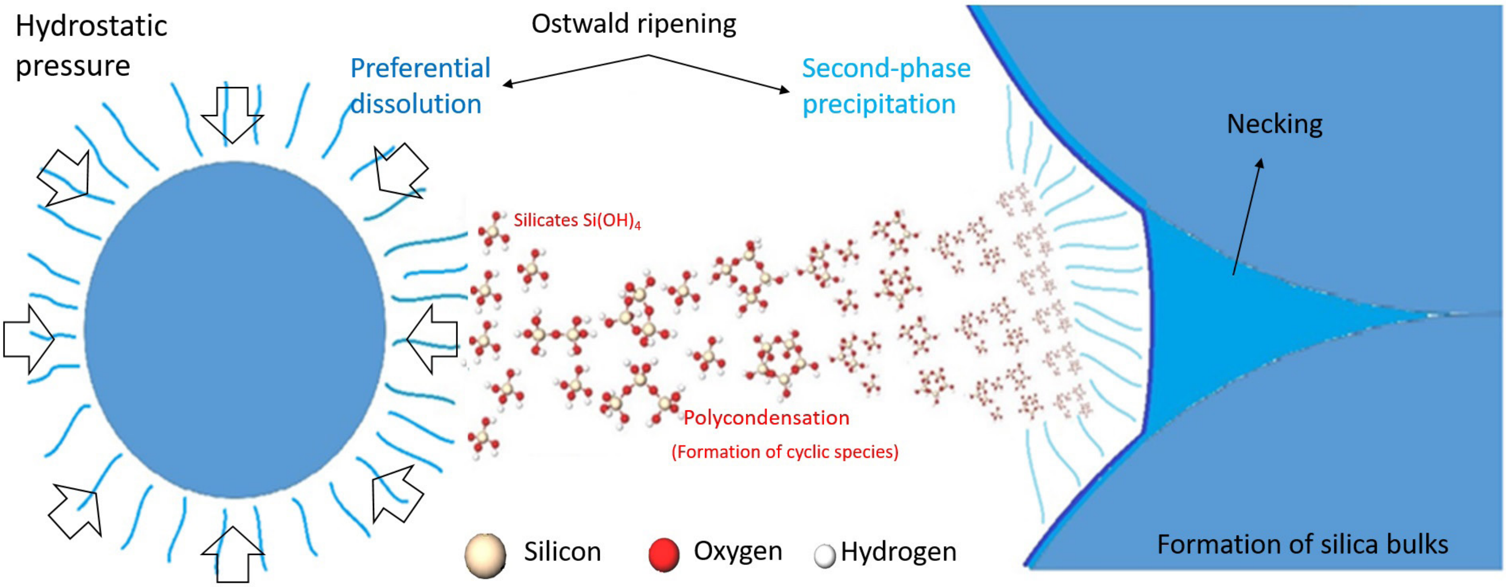
Room temperature densification of amorphous silica (nanoparticles and microbeads) is developed through the application of hydrostatic pressure (HyPS) on a silica-water suspension. This method takes inspiration from the well-known biological silicification (bio-sintering) of marine life forms silica-based skeleton in terms of dissolution, precipitation, and hardening mechanisms. Cold sintering processing (CSP) based on uniaxial pressure is taken as a benchmark. Starting from a green-body relative density of 70%, densification exceeding 99% is achieved by adding distilled water to an amorphous powder under a hydrostatic pressure of 450-600 MPa for 5-30 minutes. A thorough model of densification aiming to define the influence of the sintering parameter (i.e. pressure and soaking time) was based on the consolidation of fused silica bulk microbeads. The observation of the sample microstructure led to the conclusion that the densification is attained through a preferential precipitation of a second-phase from silica dissolution under hydro-pressure (Figure 1). Precipitation is governed by minimization of the surface energy, which is the driving force of the Ostwald ripening mechanisms. Transmission electron microscopy, NMR, and FTIR spectroscopy reveals the chemical steps leading to the final bio-sintered compound and the analogies with bio-silicification. TGA/DSC thermal analysis defined the role of physical and molecular water in the sample microstructure.

Keywords: Bio-sintering, Hydro-pressure processing, Ostwald ripening



ABS 116

INVESTIGATING CLEANABILIYTY PERFORMANCE OF DIFFERENT TYPES OF PORCELAIN STONEWARE TILES

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Porcelain stoneware tiles are fully vitrified materials with excellent technical characteristics are widely used in domestic environments and in public and industrial environments. It is expected that porcelain tiles maintain their functional characteristics in all working conditions during its lifetime.

Cleanability can be defined as a performance characteristic of the surface of a material and the ease of removal of stains on the surface of the tile by various substances or the removal of stains completely. Another important point is the consideration of the resistance to staining and its cleanability on the abraded surface. Since the abrasion resistance of the tile varies according to the surface morphology, size and distribution of the pores, the abrasion resistance and therefore the cleanability properties of the products vary from product to product.

In this study, different types of porcelain tiles were provided from a local tile producer. Tiles were stained with different staining agents in order to represent a real working life. Stain contact time, amount and type of staining agents were determined for each type of tile. Tiles that not showed easy clean properties were further examined in terms of their surface morphology and production method. Tiles that stains removed easily were abraded (ISO 10545-7, 12000 rev.) and stained with the same staining agents and applied same cleaning procedures.

Profilometry (values of roughness, Ra) of the surface and electron microscopy were employed in order to describe the topography, distribution and orientation of crystals and the defects before and after abrasion of the tiles. Cleanability performance of tile surfaces was observed before and after abrasion and a cleanability matrix was created.

The resistance to stains of the tiles was found to be related with surface roughness and morphology (pore structure and crystal type, the crystallinity of the glaze and the morphology of the crystals at the surface of glaze) and associated to the type of manufacturing method of the tile. It was observed that cleanability was strongly influenced by the actual state (structure) of the ceramic tile surface which may vary with use and wear according to production type of tiles.

Keywords: Cleanability, Morphology, Porcelain Stoneware Tiles

ABS 113

IN SITU FOURIER-TRANSFORM INFRARED SPECTROSCOPY EVALUATION OF FLY ASH BASED ALKALI ACTIVATED MATERIALS WITH DIFFERENT TYPE AND AMOUNT OF PRECURSORS

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Alkali activated materials (AAM) are recognised as promising alternatives to technical ceramic and building materials. There are several potential precursors for AAM production such as various slags, metakaolin, fly ash (FA), calcinated clays and natural pozzolans [1]. Present research considers the valorization of a FA generated as waste in a Slovenian Thermal Power Plant. FA is a coal combustion product that is composed of the particulates that are driven out of coal-fired boilers together with the flue gasses. It is already used as an additive in Portland cement or brick industries. Its chemical and physical properties vary according to the coal source and thus numerous investigations are required in order to clarify the reaction mechanism of FA based AAM [2].

Mechanical and chemical properties of AAM are strongly dependent on the precursor, activator, the curing regime, particle size etc. The objective of this study was to evaluate the influence of different type and amount of precursors on mechanical properties (bending and compressive strengths) of hardened FA based AAM. For better understanding of the alkali activation process also in situ Fourier-Transform Infrared spectroscopy (FTIR) was carried out.

After characterization of FA by means of XRF, XRD and particle size analysis various mixtures with different slag/activator ratios were prepared (activator/FA = 0.40; 0.40 and 0.37 where the activators were NaOH; Na2SiO3; and mixture of Na2SiO3/NaOH respectively). Mechanical strengths were determined at an age of 4 days after curing at a temperature of 70 °C. The values of bending strength measurements were between 1 to 9 MPa whereas compressive strength measurements were between 30 and 60 MPa. With the FTIR in situ measurements two phenomena were followed: i) the decrease of the H2O bands intensity (~ 3300 and 1640 cm-1), and ii) the displacement of the main peak between 950 and 1000 cm-1 attributed to the Si-O-Si/Al stretching vibration and is altering due to the Si/Al/O network rearrangement during the alkali activation process.

Acknowledgments
Slovenian Research Agency is acknowledged for the project grant J2-9197. Project No. C3330-17-529032 “Raziskovalci-2.0-ZAG-529032” was granted by Ministry of Education, Science and Sport of Republic of Slovenia. The investment is co-financed by the Republic of Slovenia, Ministry of Education, Science and Sport and the European Regional Development Fund.

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Keywords: fly ash, mechanical properties, Infrared spectroscopy

ABS 928

RESEARCHES ON MECHANICAL PROPERTIES AND FRACTURE BEHAVIOR OF MgO-C REFRACTORIES BASED ON WEDGE SPLITTING TEST AND DIGITAL IMAGE CORRELATION: INFLUENCE OF GRAPHITE CONTENT

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A thorough understanding of the mechanical properties and fracture behavior was the prerequisite for optimizing the thermal shock resistance of MgO-C refractories. Among many methods of studying fracture behavior, Digital Image Correlation (DIC) method was an effective tool for measuring the displacement field and deformation field of materials and widely used to characterize the fracture process of materials due to its advantage of non-contact and universality. In the present work, wedge splitting test combined with digital image correlation method was utilized to study the influence of graphite content on mechanical properties and fracture behavior of MgO-C refractories. The result of wedge splitting test showed that with the increase of graphite content from 12wt% to 20wt%, the elastic modulus and nominal notch tensile strength of MgO-C refractories decreased gradually. Meanwhile, the specific fracture energy and characteristic length increased from initial 283.09J/m2, 112.33mm to 374.12J/m2, 172.69mm, accordingly, which indicated that increasing graphite content led to a reduction in brittleness and an improvement of thermal shock resistance of MgO-C refractories. In addition, the result of DIC analysis showed that the crack initiated before the peak load and propagated rapidly once the force exceeded the peak load for MgO-C refractories with different graphite content. Besides, the ultimate Crack Mouth Opening Displacement (CMOD) and Length of main crack (Lm) increased as the carbon content increasing, which indicated that MgO-C refractories with higher graphite addition had better ability of against deformation damage. Also, it was suggested from microscopic fractographic analysis that the improvement of thermal shock resistance was positively correlated with the increase of interfacial crack propagation.

Keywords: MgO-C refractories, Fracture behavior, Digital image correlation

ABS 35

DETERMINATION OF RECYCLING PARAMETERS OF CERAMIC SLUDGE AND ITS USABILITY IN CERAMIC TILE PRODUCTION

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The rapid increase in the world population, limited resources and environmental pollution caused by the waste have further increased the importance of recycling in the 21st century. As with all production sectors, efficient use of limited resources and recovery of wastes are aimed at preventing environmental pollution and reducing costs by reducing the use of purchased raw materials. Thus, high value-added environmentalist materials can be produced. In the ceramic sector, waste sludge may be formed during the production and these are collected in the treatment facilities. Polyelectrolyte and $Al_2(SO_4)_3$ are added as flocculants during the collection and concentration of the incoming waste sludge. After these processes, it must be disposed of due to the chemicals harmful to the environment in the waste sludge. However, its viscosity is very high due to the precipitating chemicals in it, and therefore the sludge has no flow. It is aimed to reduce the limited raw material usage, to eliminate the environmental damages caused by the wastes and to recover the waste sludge from the factory for the production of new ceramic tiles with high added value. X-ray fluorescence (XRF) spectroscopy and X-ray diffraction (XRD) analysis of the waste sludge from the factories in Çan district of Çanakkale will be characterized by determining their chemical properties, passing through sieves with different pore diameters and determining the size distribution of the waste sludge by particle size measurement device. Various parameters such as the solids, the amount of water, the mixing time, the amount of Na_2SiO_3 will be examined in order to reach the appropriate viscosity values of the waste sludge. Prepared tablets from waste sludge which are brought to appropriate viscosity values will be prepared and their characteristics such as color values (L a b), shrinkage, water absorption, and strength will be determined. Then, the prepared sludge will be prepared using different amounts of raw materials in the production of ceramic tiles, and the rheological properties of the sludge will be influenced as well as the characteristics of the baked tablets such as color values (L a b), shrinkage, water absorption, and strength. Finally, XRF, XRD, sieve analysis of the raw material to be produced ceramic tile will be carried out for the most suitable formula. The raw, dry and baked strengths, mercury densities, percent water absorption values, shrinkage values, color values (L a b), dilatometer measurements and deformation values of the ceramic tiles prepared will be compared in the same temperature and time burning conditions for the ceramic tile in standard production. Thus, the most appropriate physical and chemical parameters will be determined for the recovery of the raw materials that are released as waste in the factories.

Keywords: Recycling, Recycling of ceramic sludge, ceramic tile

ABS 22

CERAMIC RAW MATERIALS IN RWANDA: AN EXPLORATORY STUDY FOR CLAYS AND FELDSPAR

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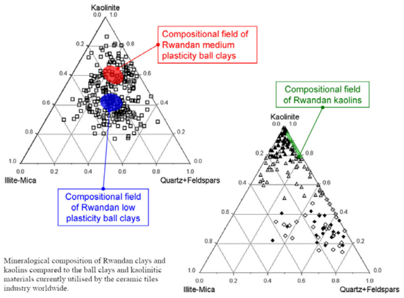
The use of ceramic raw materials have been growing in recent years as a consequence of the increasing ceramic output worldwide. Besides, ceramic industry has known a considerable product and process innovation that fostered the development of novel typologies and applications, implying peculiar technological requirements of ceramic raw materials. Thus, the technological requirements of ceramic raw materials are ever stricter in terms of rheological and compaction behavior as well as refractoriness and firing colour. This work is focused on the search for ingredients of ceramic bodies coming from Rwanda with technological properties suitable for the manufacture of building materials (floor and wall tiles, sanitaryware). The main goal is to get an overview of industrial minerals deposits available in Rwanda that can be utilized as ceramic raw materials. The prospection for suitable mineral deposits (clays, kaolin, feldspar and carbonates) and sampling were accomplished by the Rwandan Geological Survey. Nine clays, eleven kaolins and three feldspars were selected and their mineralogical and chemical composition, particle size distribution, rheological behaviour, plasticity (Atterberg limits), fusibility, colour and ceramic behaviour were determined. The Rwandan clays are characterized by a rather uniform composition, where kaolinite (30-65wt%) predominates over illite (10-30wt%) and quartz (15-30wt%) with minor amounts of feldspars (<10wt%), iron oxy-hydroxides (<5wt%) and titania phases (<2wt%) occur. According to their mineralogical features, particle size distribution (40-75% of fraction below 2 µm) and Atterberg limits, these raw materials can be considered ball clays with a low to medium plasticity. Rwandan kaolins are mostly pure raw materials, where kaolinite group minerals represent over 80% of the ore and the remaining part is essentially quartz (plus some muscovite). There are relatively fine-grained kaolins (>60% of fraction below 2 µm) with a fair degree of plasticity. Such features classify these deposits as high grade kaolins which are suitable for ceramic applications. Rwandan feldspars are characterized by a low amount of contaminants ($Fe_2O_3+TiO_2<0.3\%$) and a variable content of feldspars, ranging from about 70 to 95wt%. Two types of feldspathic fluxes are found: a high grade sodic feldspar (comparable in composition and fusibility with the best sodic fluxes on the market, e.g. Turkish Na-feldspar) and a mixed sodic-potassic flux with ~30wt% of quartz (which composition and fusibility are analogous to many widely used ceramic fluxes). On the basis of composition and technological properties, the mineral resources here evaluated can feed the industrial production in Rwanda of ceramic tiles and sanitaryware.

Keywords: raw materials, technological performances, ceramic behavior



Mineralogical composition of Rwandan clays and kaolins compared to the ball clays and kaolinitic materials currently utilised by the ceramic tiles industry worldwide.

ABS 21

DEGRADATION, DUE TO MILLING, OF Cd, Se, Pr AND Sn BASED PIGMENTS FOR CERAMIC INKS

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Ceramic tiles and slabs production technology was strongly affected, in the last decade, by a real technological revolution: decoration of surfaces by Ink Jet.
Thus brought the necessity of a strong research effort on the formulation of the inks, mostly on their liquid part, to optimize their behaviour during storage in tanks, into the printer's tubes, within the print heads etc., increasing very deeply the knowledge of the chemical, physical and rheological properties of these systems.
Attention was also devoted to the solid part of the inks, the pigments, mainly to increase their colour Gamut, and many attempts were done to try to increase the size of their grains, according to the printing resolution, to avoid major problems of grinding.
According to all of these parameters, there were various attempts to produce ink with pigments of several µm of average grain size, but the technology is now generally set on inks having the solid part at a grain size < 1 µm, with many evolution towards some hundreds of nm.
Some pigment, however, may have a particular sensitivity to grinding, due to their structural weakness, and it was interesting to study their behaviour and degradation on milling.
For this purpose, 4 main pigments were chosen: red Cd(S,Se), yellow CdS , yellow Zr/Pr and pink Cr/Sn.
They were ground into an industrial micro-sphere mill at three different grain size: among 2,0 and 4,0 µm, as for traditional decoration lines, among 0,5 and 0,6 µm, as for normal ink jet inks, and among 0,30 and 0,35 µm, as an optimal grain size range for high definition decoration.
These suspensions were studied as:

- Grain size distribution by laser diffraction
- Thermal stability by TGA-DTA
- Chemical composition by XRF
- Structural habit by XRPD, Rietveld XRD
- Powder morphology by FEG-SEM

Inks were, then, applied on ceramic tiles and fired in industrial conditions. On the final products

Colour development by Colorimetry
Chemical stability by ISO 10545.13 and .15 + ICP-AES on solutions
were also checked.

Obtained results permitted to evaluate the morphological and structural modification on milling, and their loss of colouring power, their decreased resistance to chemicals and the increasing tendency to release cations, potentially dangerous for the ambient: this could bring problems in the re-use of these materials and also in their disposal.

Keywords: Milling, Se, Cd, XRDP

S09

CERAMICS IN CULTURAL HERITAGE AND ART

INVITED LECTURES

ABS 388

RECOVERY, RESTORATION AND CHARACTERIZATION OF A NUCLEUS OF PORCELAINS FROM THE GINORI MANUFACTURE IN DOCCIA, BELONGING TO MIC FAENZA

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In 2017, the project of enhancement of the group of ceramics recovered after the destruction of the MIC Faenza, during the Second World War, started. This nucleus of pre-war porcelains has been the subject of a detailed activity of selection that has involved the students of the Master Degree Course, single study cycle, in Preservation and Restoration of Bologna University – Ravenna campus. The recovery and consecutive restoration of a rare cist, decorated with printed motives, part of the Isola Manara's set, dated back to 1749-1750, and of a coeval cache-pot with historiated bas-relieves decorations, has been presented.
Alongside these important recoveries, the experts carried on a study of characterization of the porcelains made in Doccia, during Carlo Ginori's management (1735-1757), examining the exemplars of the Faenza Museum collections. Beside the already mentioned works, they included in the research the sculpture of Cupid and Psyche dated back around 1547-1548 and the double wall coffee pot made around 1745-1750. Such characterization, that includes chemical mineralogical analysis and examination through the electronic microscope, has been based on the will to define the recipe of the Doccia porcelain, developed in the manufacture production. Another interesting aspect to verify is represented by the eventual influence on the Ginori's recipe, of the coeval European productions. Some sources suppose that the first Doccia production was the result of technological influences from another European manufacture, more than the result of the experimentations carried on by Carlo Ginori. In this case, the foreseen researches on the materials could result decisive.

Keywords: Ginori porcelain, restauration, chemical mineralogical testing

ABS 399

ARCHAEO-CERAMIC 2.0: INVESTIGATING ANCIENT CERAMICS USING MODERN TECHNOLOGICAL APPROACHES

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Since the first attempts to the petrographic analysis on pottery, a multitude of archaeometric studies have been carried out in the last century to solve important issues on provenance, production technology, function, dating and conservation of ancient ceramics. According to the scientist background, when the investigations were done, destructive vs. non-destructive analyses and the purpose of the research, numerous analytical methods typically used in various disciplines have been applied. In the last years, the advancement of modern instruments, the accessibility to facilities in the past devoted particularly to basic research or available only in few structures across the world, the development of accessible and fast processing software, as well as of a new class of scientists with important both analytical skills and sensibility for the cultural heritage, have been at the basis of a modern era of archaeometric studies.

This contribute focus on the use of innovative approaches to solve archaeological issues, reporting some examples of new methods applied to mineralogical, petrographic and chemical analyses.

The traditional microscopic characterisation of ceramic pastes, for instance, can now be easily coupled with quantitative analysis of abundance and size distribution of their textural features, through the application of digital image analysis. This method, applied to images acquired by polarised transmitted light microscope, scanning electron microscope in back-scattered mode and microchemical mapping, can quantitatively and quickly describe production recipes, contributing in the definition of the pottery production choices and evolution over the time.

As for the mineralogical analysis, the possibility of simultaneously processing numerous X-ray diffraction patterns by statistical tools, such as the cluster analysis on raw data, is another example of a modern way of analysing ancient pottery and interpreting, with an objective comparison method, possible differences or analogies in the production recipes and/or firing technology of groups of ceramics. Moreover, the modern micro-diffraction techniques, both using conventional (X-ray tubes) and unique sources (synchrotron light), also coupled with micro-Raman spectroscopy, allow to determine the mineralogical composition of small-sized phases both in ceramic bodies and slips/glazes, supplying important information on the production technology and possible post-deposition processes.

As for the provenance issue, especially on fine ware, relationships between also far way communities/societies can now be constrained not only on the basis of conventional bulk chemistry, but also by isotope analysis.

These new methodological approaches give rise to a modern concept of archaeometric analysis on ceramic materials, that can be defined as archaeo-ceramic 2.0.

Keywords: archaeometry, new modern approaches, archaeo-ceramic 2.0

ABS 79

SILVER NANOPARTICLES IN GLASS AND GLAZES - YELLOW STAINS AND LUSTERS

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Both historical yellow silver stain and luster decorative techniques consist of a mixture of silver salts with clay or ochre, which forms, after firing, a coloured or metallic-coloured layer obtained by the formation of silver colloidal particles inside the glass or glaze substrate. The obtained colour depends on several properties and reactions, related to the substrate and paint composition and also with the time and temperature of the annealing. The technology for the production of this colours and reflections is still not completely explained and even nowadays their reproduction is a great challenge.

This study was centred on the analysis and reproduction of recipes found in historical treatises to better understand production processes of both yellow stain and silver lustre. The analysis of treatises resulted in the collection of recipes from the 14th to the 19th centuries, belonging to Antonio da Pisa, André Félibien, Johannes Kunckel, George Bontemps, Bologna Manuscript, and Marciana Manuscript.

An important testimony of the luster production is the treatise The Book of the Hidden Pearl by Jazbir Ibn Hayyan (8th century - Abbasid caliphate). He was considered in Europe during the Middle Age as the father of alchemy and the first person who separated sulphuric and nitric acids. Between his recipes, 118 concern luster painted.

Recipes of lustres and yellow stain were selected and their viability to produce satisfactory results was tested. The characterization of the reproduced recipes was done via UV-Vis Absorption and Reflectance Spectroscopy, Particle Induced X-ray Emision, X-ray Diffraction and SEM. These analyses allowed us to comprehend the difference in obtained tones, relating those with the paint compositions.

Keywords: Silver nanoparticles, Glazes and Stained glass, Technical Art History

JOHANNIS KUNCKELII,
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S09

CERAMICS IN CULTURAL HERITAGE AND ART

ORAL PRESENTATIONS

ABS 848

APPROACHING MOBILITY THROUGH POTTERY ANALYSIS IN THE BALEARIC ISLANDS DURING THE BRONZE AGE

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Pottery is one of the most durable and abundant artifacts in the archaeological record, thus becoming a significant source of data for addressing mobility in ancient societies. In this article I deal with the analysis of the mobility of people and ideas in the Balearic Islands during the Bronze Age by means of two strategies:

1) From the study of the technological choices identified in the hand-made pottery produced in several archaeological sites from Mallorca, Menorca, and Formentera. In this way, this study demonstrates -through the use of certain paste recipes- that the Balearic Islands were not totally isolated in the Bronze Age but socially connected.

2) From the analysis of a pottery assemblage related to an anchorage site. The prospecting works carried out in the archipelago suggest that such connectivity was developed through a network of coastal settlements that made possible coastal navigation throughout the archipelago. However, there is a lack of data regarding how such mobility was articulated and the role played by these archaeological sites. In this context, I conducted diverse archaeometric analyses (petrology, X-ray diffraction, and X-ray fluorescence) on a set of large storage vessels recovered from a coastal anchorage site in order to understand the way in which this network of coastal settlements was organized. Results allow to state that there is a greater degree of variability in the ceramic record present in this kind of coastal anchorage sites in comparison with the pottery from habitat sites. In this way, the chemical data suggest that such anchorage sites were mainly managed by specific archaeological sites, even though they also received materials from other locations.

In conclusion, the archaeometric study of the pottery has provided interesting information about the way certain coastal archaeological sites were managed and the social significance of knowledge transfer related to pottery production between the different islands of the archipelago.

Keywords: Bronze Age Pottery, Mobility and knowledge, Petrography, XRD, XRF

ABS 845

INTEGRATED ANALYTICAL TECHNIQUES ON POLYCHROME GLAZED TERRACOTTA FROM THE FRIEZE OF THE "SPEDALE DEL CEPPO" IN PISTOIA

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This paper shows the results of the scientific investigations carried out on the materials of the glazed polychrome frieze of the ancient hospital, the "Spedale del Ceppo" (fig. 1) in Pistoia. The architectural development of the building goes from 13th to 16th century, when Leonardo Buonafede, a catholic bishop and director of the Spedale, commissioned a frieze for the upper part of the façade. The frieze is an interesting example of glazed polychrome terracotta representing Five Theological Virtues and Seven Corporal Works of Mercy. Santi Buglioni made six of the seven sections from 1526 to 1528 century, while the seventh section, Give Drink to the Thirsty, for some reason was completed only in 1586 by Filippo Paladini. It is important to note that glazed and not glazed kiln, some of them representing Give Drink to the Thirsty, were found in an old well in the North-West area of the Spedale. Nobody knows what happened to these burned and over fired materials and who made them. The recent restoration of the frieze, carried out in 2015, suggested to carry out an integrated scientific campaign based on the use of both non-invasive and micro-invasive techniques, with the aim to acquire information on materials, technique and state of conservation in order to project an adequate restoration treatment. On first, imaging exams like visible light photograph, UV fluorescence, IR reflectography and false colour IR were carried out. Reflectance spectrometry in the visible range (vis-RS), colorimetry (CM) and energy-dispersive X-ray fluorescence spectroscopy (ED-XRF) were performed in order to gather as much information as possible on the frieze by minimizing the sampling. As a second step, after carefully collecting a representative set of micro-fragments, the frieze and the wasters were analysed by several analytical techniques: optical microscopy (OM), X-ray diffractometry (XRD), environmental scanning electron microscopy with energy dispersive spectroscopy (ESEM/EDS), FTIR and micro-Raman spectroscopy. The methodologies used allowed testing the usefulness of a new method combining non-invasive and micro-invasive tools to study the polychrome glazed terracotta, highlighting the importance but also the limits of non-invasive analysis. The composition of clay bodies allows us to hypothesize that Santi Buglioni used marly clays taken in the Arno river to produce the six friezes. In the seventh frieze Filippo Paladini used iron-rich non-carbonate clays comparable with Montelupo raw clays. The chosen approach was useful to obtain an exhaustive characterisation of glazed coatings made by Santi Buglioni as well as those made by Filippo Paladini, showing different executive techniques and conservative problems.

Keywords: glazed polychrome terracotta, Santi Buglioni, non/micro invasive exams

ABS 818

INDUSTRIAL PRODUCTION OF WHITE EARTHENWARE IN THE JOHNSTON-VIEILLARD MANUFACTORY (19th CENTURY): RECIPES EVOLUTION AND PRODUCTION STRATEGIES

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The aim of this paper is to present research conducted on the ceramic productions of a French ceramic manufactory in Bordeaux. The Johnston-Vieillard manufactory produced, between 1845 and 1895, a special type of ceramic called “white earthenware”. Although general documents remain (such as ceramic treatises, World Exhibition’s catalogues, lawsuits, correspondences), factory archives (that were either lost or destroyed) are severely lacking in order to document the production techniques (choice of raw materials, recipes, firing conditions, division of labor and life in the manufactory, …). Recently, a lot of pieces and remains of white earthenware (wasted materials and elements used at the different stages of the chaîne opératoire) were discovered during an excavation performed in the ancient factory area. In the present study, we focused specifically on the modifications over time of white earthenware production.

We examined six groups of sherds representative of different production periods of the factory. These sherds came from the available and abundant wastes found during the excavation located in the ancient waste dumps of the manufactory. A total of 150 fragments – 70 biscuits and 80 glazed white earthenwares – were selected for analysis. As a matter of fact, composition of bodies and glazes were investigated using a combination of analytical techniques that included Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS), Particle Induced X-Ray and Gamma Emission (PIXE-PIGE) and X-Ray Diffraction (XRD).

Analyses showed significant differences on chemical composition of glazes and bodies during the different stages of the factory life. Thus, it is possible to make assumptions concerning the recipes used for paste and glaze during the different chronological periods.Of course, these recipes are compared to those available in the literature of the 19th-century. Finally, hypothesis about adaptability of the glaze to the paste are discussed, in particularly, the correlation between the modifications of glazes and bodies composition with the variations of the coefficient of thermal expansion.

The aim of this work is to contribute to document an industrial production of white earthenware throughout the 19th-century. Results obtained on the characterization of the ceramic production technologies and on the modification over time of the recipes (glazes and bodies) will be presented.

Keywords: white earthenware, recipes, PIXE-PIGE

ABS 796

TULLIO D'ALBISOLA BEYOND FUTURISM: CERAMICS ABOVE ALL

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This paper focuses on the figure of Tullio Mazzotti, better known as Tullio d'Albisola (Albissola Marina 1899-1971). Even though his role as a protagonist of the Futurist movement, especially in a new and modern ceramics proposition, has already been addressed since the 1980s, by prominent scholars such as Enrico Crispolti and Franco Sborgi, a deeper study about Tullio d'Albisola still lacks. Thanks to the unique opportunity to match data from the private archive of the artist and those collected in public libraries and archives, such as the Beinecke Rare Books Library (Yale University), the Museum of Modern and Contemporary Art in Trento and Rovereto (MART) and the International Museum of Ceramics in Faenza (MIC), this paper will present the outcome of a first survey, carried out upon Tullio d'Albisola's contribution not only to the sake of Futurism, but also to the freedom and the dignity of ceramics (made by artisans, as well as artists) within the new, modern, urban society of the 1900s. Beyond the role of reference for the Futurist movement, Tullio d'Albisola has always cultivated his own passion in ceramics traditions, techniques, history and critics, becoming one of the most estimated expert in ceramics matter in Italy and beyond, establishing correspondences and collaborations with colleagues in Italy but also with pivotal artists engaged with ceramics such as Lucio Fontana, Pablo Picasso, and many others.

Keywords: Tullio d'Albisola, Futurism, Art and Design

ABS 763

GLAZED CERAMIC TILES: LABORATORY TESTS USING CONTACTLESS VIBRO-ACOUSTIC DIAGNOSTIC TOOLS TO REVEAL GLAZE DELAMINATION DECAY PROCESSES

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The integrity of the surface painted glazed layer has a great impact on the safeguard of the artistic glazed ceramics, also involving the transmission of their intangible aspects. Glaze delamination and spalling is a severe problem for these artworks; revealing the occurrence of early decay processes represents a highly desirable possibility helping the preventive conservation. The authors wish to explore the possible ways to pursue this objective, attempting to non-destructively detect thin glazed delaminations when they are not yet visible to the naked eye.

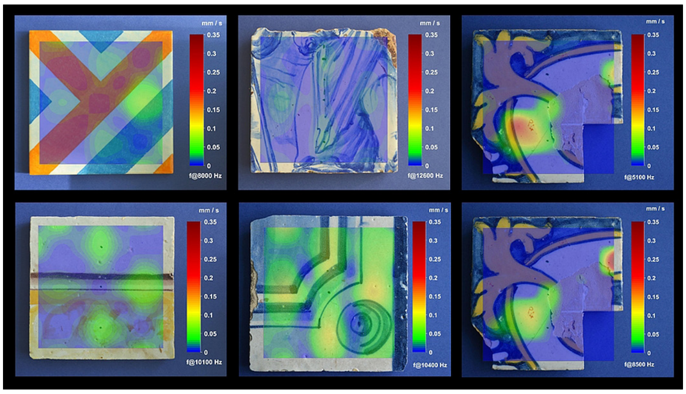
In recent research studies, contactless vibro-acoustic methods allowed to identify sub-surface artificial cavities, a few-hundreds microns deep, in laboratory models and natural delaminations in historical glazed ceramic tiles, by inducing the defect to vibrate by means of an external acoustic pressure field. The present study adds further insight to this issue by analysing a greater number of real tiles, mainly focusing on some apparently integer samples with respect to a delaminated one.

The samples belong to a little collection of antique Portuguese azulejo dated between the 17th and the 18th century. Additionally, a modern tile is used as reference. In these laboratory tests a contactless acoustic wave source in the audio frequency interval is employed to induce the vibration in the sample, whilst a Laser Doppler Vibrometer (LDV) measures the vibration velocity of the sample's surface.

The experimental data are displayed as 2D images of the vibration velocity at the most significant frequencies. The characteristic normal modes of vibration clearly characterize the undamaged tiles, with low velocity values and geometric patterns, being the sample free to vibrate as a whole according to its preferential natural modes. Elseways, confined spots with high velocity values indicate the position and the extension of glaze delaminations in the damaged tile. The frequency profiles of the most representative points provide further information: small and narrow peaks at specific frequencies in the first group of samples; broad and high velocity peaks in the second one.

Laser Doppler Vibrometry is particularly powerful to evaluate the conservation state of glazed ceramic tiles due to its high spatial resolution and non-invasiveness, although an accurate device-sample alignment and the data interpretation from expert operators are important requirements. The present study examines the vibrational characteristics of glaze delaminations in a damaged tile, and compares them with those found in the undamaged tiles highlighting the main differences. The experimental results help a better understanding of the most appropriate methods, the optimal experimental settings and data analyses to adopt for approaching an ever growing effectiveness in the detection of the early delamination processes.

Keywords: Glaze delamination, Vibro-Acoustic Imaging, Non-destructive diagnostics



ABS 759

NEW ATLAS OF PREHISTORIC CERAMIC FABRICS

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The Atlas is a new general standardised description and classification of the petrographic characteristics of Central Mediterranean pre-prehistoric pottery. One goal in studying pottery is to define significant taxonomic units, which can describe a specific potter's behaviour (the technological 'recipes'). The Atlas is a tool that can be used to compare the different components of the ceramic pastes and to check possible provenance of non-local pots. It is an outcome of the archaeological and archaeometric database Wikipottery, an interdisciplinary collaboration between Modena e Reggio Emilia University, CNR-ISMA (Roma) and Preistoria Attuale (Cannavò and Levi 2018, Levi et al. in press).

The Atlas includes -so far- 1825 samples from 92 sites across Italian peninsula and islands. The majority of the pottery belongs to the traditional Impasto ware: coarse and therefore suitable for petrographic investigation. The new general classification is organized in two levels: at a more general one the Groups are linked to geological/lithological environments. In the frame of the Groups, the Fabrics are then defined according to the main components and other characteristics (minor components, size and abundance of clasts and the matrix). 163 petrographic Fabrics have been defined

This paper focuses on an iconic case study from the Atlas: Lipari in Aeolian Islands, a strategic location in the Central Mediterranean characterized by 5000 years of continuous inhabitation (from the Neolithic to the Final Bronze Age: 6th-1st mill. BCE.). 380 samples have been selected and 33 (locally made and imported) fabrics have been identified at Lipari.
Local products are well distinguishable and a single main local Fabric characterizes the entire sequence (more than 150 samples), pointing to a noticeable continuity of tradition. Other local Fabrics are linked to specific productions showing a certain degree of creativity. Toward the end of 2nd millennium, several local products were locally made with local volcanic temper mixed with imported clay. Numerous imported Fabrics have been also identified showing different sources and origins.

Lipari's case study show the effectiveness of this methodology to reconstruct -in a diachronic perspective- social organisation of production, technology, trade, function, environment, complexity and change in ancient societies.

Keywords: Atlas of Fabrics, prehistory, pottery

ABS 749

IMPERIAL AND LATE ANTIQUE CERAMIC PRODUCTION TECHNOLOGY AT MONTELABATE IN THE UPPER TIBER VALLEY

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The paper will present the results of new research into Roman coarseware production technology, trade and exchange in the upper Tiber valley in Central Italy between the first century to the fifth century AD.
The study focuses on the characterization of the sources of raw material for ceramic production, using geotechnical methods (Atterberg limits and grain size distribution), XRF, XRD, TG-DTG and FTIR analyses. The interpretation of the ceramic manufacturing technology, using the same analytical techniques, allows the definition of the ceramic production process at the important manufacturing centre of Montelabate (Perugia, Italy). The workshop, which comprised six kilns, produced amphorae, coarseware and tiles, also offers an interesting model for the study of firing technology and modifications in kiln structures using mud-bricks, which have also been analysed in order to determine the continuity and changes in the exploitation of clayey resources.

Keywords: Raw material characterization, Analytical methods, Roman ceramics technology

ABS 694

CERAMIC PRODUCTION IN THE PLAIN OF PAESTUM (ITALY): FIRST RESULTS OF AN INTERDISCIPLINARY PROJECT

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The Lise Meitner project Ceramic production in the plain of Paestum investigated the ceramic production from the Archaic period to the Roman conquest in one of the most important archaeological regions of the Mediterranean. The area is located in the plain of the Sele River, southern Italy, where intense intercultural and socio-economic exchanges occurred between the Greek colony of Poseidonia/Paestum in the south and the Etrusco-Italic sites of Pontecagnano and Fratte in the north. However, until recently, our knowledge of pottery production sites and exchange activities in this area remained limited. The research intended at answering these questions via an interdisciplinary approach between geologists and archaeologists of Austrian and Italian institutions.

More than 370 samples from the major sites and sacred areas in the territory, belonging to different ceramic classes of coarse ware (common ware and figural terracotta) and fine pottery (glazed and miniature pottery), were analysed via mineralogical-petrographic techniques for investigating the technological features and the provenance of ceramic productions, also by the comparison with local. Production indicators, represented by remains of craft activities, were analysed to define the compositional features of local products and establish a standard of comparison.

One of the most interesting results is the clear distinction between coarse ware produced in the two sectors located north (Pontecagnano and Fratte) and south (Paestum) of the plain respectively. Ceramics from the northern sector are characterised by a larger amount of volcanic inclusions, as these sites are closer to eruptive centres of the Campania region. The chemical composition points out the use of two types of local clays characterised by different concentrations of calcium oxide. On the contrary, in the territory of Paestum coarse ware showed a chemical variability independent from the context of discovery and a petrographic composition marked by the presence of siliciclastic inclusions, associated to minor carbonate; a large group of samples slightly differs as it also contain sporadic volcanic inclusions. Even though at the moment it not easy to distinguish between productions from specific contexts in the territory of Paestum or from the city itself, their petrographic composition is fully compatible with the geological features of the area, characterised by siliciclastic and carbonate formations, along with minor volcanic deposits.

The compositional features of fine pottery from the different production sites were better recognised by comparing local clays and production indicators, thus allowing for definition of the peculiarities of local products and also for pointing out the possibility of exchange from the Greek town of Poseidonia to the Etruscan settlements located north of the Sele River. Evidence of imports from the Attic region of Greece was also highlighted by the comparison with literature compositional data.

Keywords: Plain of Paestum,Research Project,Provenance and Technology

ABS 688

PUNIC BLACK GLAZED POTTERY FROM THARROS AND OLBIA (SARDINIA): LOCAL PRODUCTIONS AND IMPORTATIONS

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Punic black glazed pottery is one of the most widespread imitation classes in Sardinia; it's mostly documented during the III sec. B.C. in all areas controlled by the Carthaginians.

This pottery is characterized by clay body generally not well purified and rich in temper, of variable color, more often grey, beige, brownish or orange. The glaze is not uniform and varies from black to gray, from brown to reddish; it is applied by immersion inside and on the upper part of the external surface. The coating is thin, easy to fall and often marked by micro-cracks. The most common forms are derived from Attic black-glazed pottery, but in the later stages of production forms derived from Campanian classes appear.

Sardinian production is portion of a more general phenomenon of Mediterranean Punic culture that is part of a very large geographical area that affects, in addition to Sardinia, North Africa, the Iberian Peninsula and only episodically Sicily.

These ceramics show variable macroscopic features and at the same time common to the different diffusion areas. The archaeological investigations suggest that they are mostly local productions, connected to the common ceramic factories, but some analyzes carried out on Sardinian pottery have shown a much more complex situation related to import phenomena from North Africa. It is evident that a macroscopic analysis alone cannot be enough to identify the different productions.

This research begun several years ago aims to gradually create and implement a database related to these ceramics in order to reconstruct as far as possible their diffusion not only of the morphological repertoire and of the technologies but also of the same artifacts.

In particular, diffractometric analyses (XRD) and optical microscopy observations have been performed on samples from the two Punic cities of Tharros and Olbia (Sardinia, Italy) to discriminate mineralogical and textural differences and to identify groups of materials with similar characteristics. Chemical analyses by X-ray fluorescence (XRF) have been performed to identify the chemical composition of the potteries, and to attest the groups obtained by microscopic and diffractometric analyses.

The results have been compared with the composition of on archaic and late punic pottery and transport amphorae coming from several Mediterranean centres (Carthage, Sulci, Toscanos, Tharros, Santa Giusta, Phitecusa).

Keywords: black glazed pottery, Punic,Sardinia

ABS 644

OXIDATION STATE ANALYSIS AND PHASE DISTRIBUTION IN ANCIENT CHINESE CERAMICS USING FULL FIELD X-RAY ABSORPTION SPECTROSCOPY

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Since the 1950's, ancient ceramics are considered with particular interest among archeological materials. Changsha kiln is one of the pioneers to master the poly-color decoration technique at high temperature, which allowed the elaboration of lead-free colored glazes. Many studies involving synchrotron-based techniques were devoted to the blue color of ceramics from the Tang dynasty, but important questions on the chromogenic mechanisms are still unresolved. The elemental composition, the size of oxide particles and their spatial distribution are thought to influence the chromatic variation. Full-field XANES (FF-XANES) technique at Fe and Cu K-edge will be employed in parallel with μ-XRF at PUMA beamline to speedily determine the Cu and Fe speciation and the elemental distribution of large areas including glaze and body. A correlative imaging methodology will be developed to process data and uncover hidden information in the spatial and spectral space. This study will help to better understand the manuftacturing processes of porcelains related to Changsha kiln and to gain a better idea about pigments provenance and trading contact across the world.

Keywords: Chinese porcelains, Poly-chromatic decor, Full Field XANES

ABS 619

USING CERAMIC REPLICAS TO UNDERSTAND ANCIENT TECHNOLOGY: NEW INSIGHTS ON THE CERAMIC PRODUCTION OF VIA DEI SEPOLCRI WORKSHOP, POMPEI

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Pompeii is one of the most important worldwide archaeological sites that preserves a precise time-frame of ancient Roman culture. A survey carried out in 2014 in Via Dei Sepolcri unearthed a ceramic workshop producing thin-walled pottery, active until a few hours before the 79 AD eruption. Here, unfired, fired, and overfired vessels along with the raw materials were found, providing a view of the entire production cycle, from the selection of the raw material to the firing operative conditions.

The study of samples was carried out to identify the raw material sources and to recognise the mineralogical assemblages produced by firing, the latter investigated by quantitative X-ray powder diffraction (XRPD) analysis using Rietveld-RIR methods.

The unfired samples, made with CaO-rich clays mixed with volcanic temper sands from Vesuvius-environs, were essential to the aims of the present research as they represent the original mixture of clayey raw material and volcanic temper. They included smectite, illite, kaolinite, and chlorite along with calcite, quartz, feldspars, clinopyroxene, and amorphous components.

As expected, hydrous phyllosilicates lack in fired vessels, characterized by a large amount of amorphous material and by the presence of high-temperature newly-formed phases. Clinopyroxene and Ca-plagioclase increase significantly from unfired to fired vessels, whereas calcite and clay minerals progressively decrease until totally absent.

Surprisingly, Pompeian ceramics did not show the occurrence of detectable gehlenite, a member of the melilite group that commonly forms in CaO-rich clays fired between 850° and 950 °C.

The lack of gehlenite has been explained by a primary effect during the firing of fine-grained clayey materials (fine ceramics do not contain significant gehlenite in contrast to coarse wares of similar mineralogy) or a secondary effect due to post-earthen alteration of metastable gehlenite (gehlenite may have undergone transformation to calcite plus smectite as a result of post-eruption alteration).

To better understand the lack of gehlenite in the Pompeian pottery, two clays found in Via dei Sepolcri workshop were treated at different temperatures and soaking times, and mineralogical transformations were evaluated by quantitative XRPD analyses. These replicas were fired from 700 to 1050°C following a rapid (1 hour of soaking time) and a slow (24 hours of soaking time) firing procedure.

Gehlenite formed in both fast and slow firings; it began to form at 850 °C for fast soaking times and at even lower temperatures (800 °C) for longer soakings. It is noteworthy that gehlenite persisted up to 1050 °C in both tests, although it progressively decreased in favour of newly-formed clinopyroxene and Ca-plagioclase. These preliminary experimental results suggest that Pompeian ceramics likely underwent post-depositional alteration; future perspective will be devoted to understanding the interactions among fluids, tephra and ceramic materials

Keywords: Ancient ceramic production, Ceramic replicas, Pompeii

ABS 609

DEVELOPMENT OF A POROUS PORCELAIN FRAPE WITH THERMOCHROMIC VISUALIZATION

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The paper presents the development of a porous porcelain frappe with thermochromic visualization for port wines, having as a partner the Institute of Vinhos do Douro and Porto.

This ceramic frappe is intended to promote the cooling and maintenance of the temperature of port wines through porous ceramic materials, consisting of a porcelain composite with sawdust addition, so as to contain, on the one hand, the similar cooling properties of the terracotta and, on the other, the resistance of materials such as porcelain.

The application of the thermochromic element makes it possible to see if the wine is at optimal service temperatures, allowing users to drink the wine in the ideal conditions and contributing to more efficient maintenance of the service.

The aim of this product is to answer the question: the synergies generated by innovation through the design and creation of an objective product, supported by partners, can lead to the dynamization of this type of ceramic industry, becoming a commercial gain for the newly revitalized factory unit of the Sociedade de Cerâmica Antiga de Coimbra?

Keywords: Design, Porcelain/Porous, thermochromic

ABS 492

A POTENTIAL METHOD OF GLAZED POTTERY DATING/ AUTHENTICATION USING THE RAMAN SIGNATURE OF PROTONIC SPECIES

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Ancient objects made of glassy silicates such as glazed pottery and glasses have always been one of the major interests in archaeological/art historical dating research. Since C-14 dating is not applicable to inorganic materials, other methods were postulated for the dating of glassy silicates based on the corrosion processes in the presence of water. H+ and H3O+ ions tend to replace the alkali ions found in the glass network on the basis of an interdiffusion process, breaking some of the Si-O-Si links. The resulting changes in the microstructure of glass induce the formation of defects, cracks and thus a corrosion layer on the surface where water molecules and hydroxyl groups are also adsorbed. The protonic species originating from water which are incorporated in the glassy silicates as a function of time give weak, more or less broad Raman features in the 2000-3700 cm-1 range and the relative intensity of the Raman signature of protonic species is considered as a potential tool for the comparative dating/authentication of glassy silicates.

For the testing of this hypothesis, glazed pottery with different origins (Chinese and Vietnamese porcelains and celadons, Islamic terra cottas etc.), time periods (ca 11th century up to the present time) and chemical compositions (aluminosilicate-based, calcium-rich and lead-rich glazes) were analyzed by Raman microspectroscopy in the scope of this study. A set of stained glass samples (13th-19th centuries) which were subjected to artificial corrosion in the laboratory conditions, already studied by IR and NIR absorption, were also analyzed as reference for the Raman signature of protonic species. H2O/OH band area extracted from the Raman spectra obtained as an indicator of intensity was used against elapsed time since production date in order to build up the empirical law of the dating method.

The results were evaluated on the basis of age, chemical composition and environmental conditions of preservation. It was mainly shown that Raman intensity of the protonic species shows a positive correlation with age for celadons and porcelains which have a lead free composition. The method also appears to be more useful to detect fakes than to provide an accurate dating.

Thus, it can be proposed as a fast and non-invasive method for the discrimination between old and modern objects (copies/fakes) in terms of authentication. The efficiency of the method is expected to be increased with the collection of a bigger number of data for very similar objects.

Keywords: dating, authentication, corrosion

ABS 454

DEPICTING THE SOCIAL ORGANIZATION OF ROMAN CERAMIC WORKSHOPS THANKS TO ANCIENT FINGERPRINTS ANALYSIS: THE CASE STUDIES OF POMPEII AND LEZOUX

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Ancient fingerprints have been recorded around the world and are apparent on various mediums, although fingerprints on ceramic artefacts are the most common. Unfortunately, there have only been a handful of academic studies using them to interpret archaeological contexts.

Combining archaeological and forensic methodologies, our works focus on two case studies aiming to apprehend the working space of pottery workshop and its social aftereffects thanks to the study of fingerprints on ceramics artefact:

In Pompeii (Italy), excavations led by L. Cavassa in the ceramic workshop in Via dei Sepolcri and of an oil lamp workshop in Reg. I, ins. 20, 2-3 highlighted the production system of an ancient ceramic workshop in the days just before the 79 AD eruption. Among numerous traces, more than 100 marks had been construed. A selection of marks on the red slip, invisible to the naked eye, have been submitted to a set of photographic technics including IR reflectography to improve their perception and our protocol. Moreover, in order to follow the products' consumption in the city, we studied fingerprints on ceramic artefacts belonging to the production kind of the first workshop.

In Lezoux (France), an excavation led by C. Driard revealed two workshops and their owners. During the early Roman Empire, the city was a very important ceramic workshop in Gaul across the Roman area, producing Terra Sigillata. This class of tableware was characterized by the stamp with the name of the manufacturer. More than 2500 fingerprinted pieces had been spotted on kiln loading sherds. Among these, a total of 85 fingerprints had been studied to shed light on this step of production.

Hence, our analysis provide the identification of the subject who had touch one or many objects, his spatiotemporal settings, his migrations between workshops, his actions, his specialization and occupation. Thus, trying to give a glimpse of his social role, authority and status within the group through matching fingerprints given that, from a fingerprint, it is also possible to estimate his age and a potential biological sex.

Keywords: Ancient fingerprints, Antiquity, Forensic

ABS 426

RELEVANT RESEARCH ON THE CERAMIC CARGOES IN WANLI SHIPWRECK

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After the Wanli shipwreck was discovered 60 miles off the east coast of Tan jong Jara in Malaysia, numerous marvelous ceramic shards have been salvaged from the seabed. Remarkable pieces of Jingdezhen blue-and-white porcelain recovered from the site represent the essential part of the fascinating research. The porcelain cargo of Wanli shipwreck is significant to the studies on exported porcelains and Jingdezhen porcelain manufacture industry of Late-Ming dynasty.

Using the ceramic shards categorization and the study of the Chinese and Western historical documents as a research strategy, the paper wants to shed a new light on the Wanli shipwreck wares classification with Jingdezhen kiln ceramic as its main focus. The article is also discussing Jingdezhen blue-and-white porcelains from the perspective of domestic versus export markets and futher proceeding to the systematization and analyses of Wanli shipwreck porcelain which bear witness to the forms, styles and types of decoration that were being traded in this period. The porcelain data from two other shipwrecked projects - White leeuw and Hatcher- were chosen as comparative case studies and Wanli shipwreck Jingdezhen blue-and-white porcelain is being reinterpreted in the context of art history and archeology of the region. The marine archaeologist Sten Sjostrand named the ship “Wanli shipwreck” because its porcelain cargo are typical of those made during the reign of Emperor Wanli of Ming dynasty. Though some scholars question the appropriateness of the name, the final verdict of the history is still to be made.Based on previous historical argumentation, the article uses a comparative approach to review the Wanli shipwreck blue-and-white porcelains on the grounds of the porcelains unearthed from the tomb or abandoned in the towns and carrying the time-specific reign mark. All these materials provide a very strong evidence which suggests that the porcelain recovered from Wanli ship can be be dated to as early as the second year of Tianqi era (1622) and early Chongzhen reign.

Lastly, some blue-and-white porcelain intented for domestic market and some bowls of blue-and-white porcelain from Jingdezhen kilns recovered from the Wanli shipwreck all carry at the bottom the specific residue from the firing process. The author makes the corresponding analysis for these two interesting phenomena.

Keywords: Wanli shipwreck, Jingdezhen kiln, blue-and-white porcelains

ABS 406

AUTHENTICATION STUDY OF MAIOLICA FROM THE MUSEO NAZIONALE DEL BARGELLO, FLORENCE (ITALY): THE POSSIBLE CONTRIBUTION OF NON-INVASIVE ARCHAEOMETRIC ANALYSES

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Objective The main objective of this study is to determine whether some maiolica wares of the Bargello Museum (Florence, Italy) are genuine ancient artefacts or forgeries made between the 19th and the 20th century. Their authenticity was questioned on the basis of their style, condition and acquisition history. This project is aimed both at 1) providing analytical data useful for their authentication and 2) developing a non-invasive, in-situ methodology to be used for authenticity studies of maiolica in museums.

Materials & Methods Three sets of glazed earthenware were studied: purported (pur.) 14th-century maiolica from Orvieto; pur. 15th-century maiolica from Deruta (Perugia); pur. 16th-century lustred maiolica. For each group, artefacts of known provenance - both ancient and dated to the 19th-20th century - were analysed as reference materials. They were characterised by optical microscopy, SEM-EDS, PIXE-PIGE and portable XRF scanning (p-XRF) giving specific attention to the composition of the pigmented glazes.
Afterwards, the biscuit of the possible fakes was authenticated by thermoluminescence (TL) and the composition of their surfaces was analysed at the Bargello by means of p-XRF.

Results Stratigraphic and compositional data of the reference materials were obtained; this was particularly important for the 19th-20th-century objects, which are rarely covered in the literature. The results showed that in some cases it is possible to discern between ancient and modern maiolica from the use of different materials in the pigmented glaze. However, 19th-20th-century potters used also traditional materials, so that it is often not possible to obtain relevant information about the period of manufacture from compositional data.
As for the questioned museum wares, TL analysis provided us with a clear authentication, discriminating between the genuine and the faked (or recently fired) objects. This outcome was also used as a reference to validate the results obtained by the non-invasive analysis of the same objects. All the main elements constituting the pigmented glazes and lustred decorations were identified by p-XRF and the results were always consistent with the TL authentication. However, only in a few cases it would have been possible to authenticate the maiolica wares solely by means of XRF spectroscopy, thanks to the presence of Cd- or Cr-based pigments.

Conclusions The Bargello maiolica of uncertain origin were authenticated. A first set of promising results was obtained by means of a non-invasive, portable XRF equipment, but a larger amount of objects should be analysed to verify the applicability of the method.

Keywords: maiolica, authentication, non-invasive analysis

ABS 945

THE LITHOCERAMIC CLADDING OF THE MODERN MOVEMENT ARCHITECTURE IN ITALY: AN UNCERTAIN FUTURE

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Italian Modern Movement architecture is characterized by the research and use of innovative, experimental and autarchic finishing materials.

Among these, one of the most interesting is lithoceramic, which was born as an Italian reinterpretation of German and Dutch klinker. Unlike other Modern materials, the performance characteristics of this ceramic material are improved over time thanks to constant collaboration between designers and manufacturers, which gives rise to architectural results of remarkable aesthetic and technological quality.

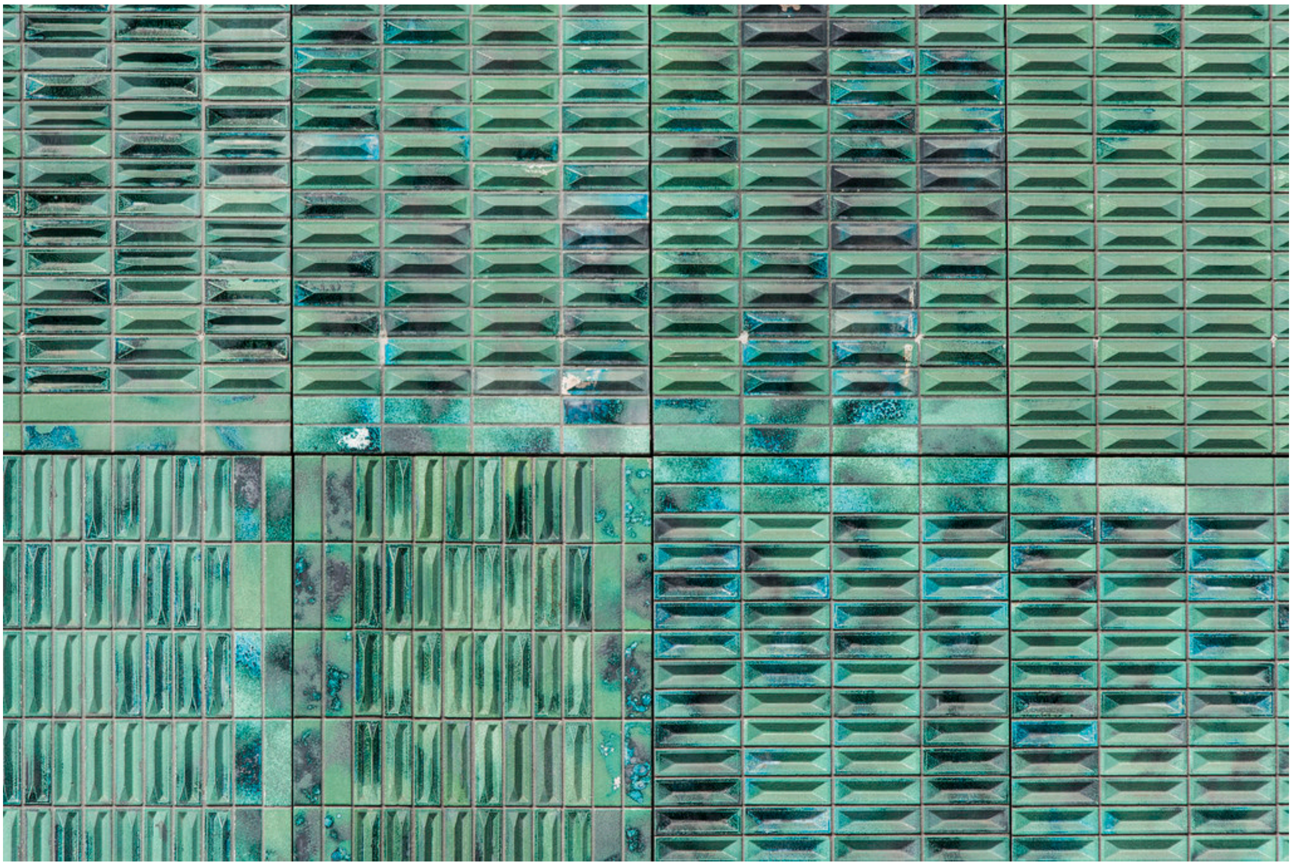
Between the 1930s and 1970s, lithoceramic claddings spread to the main Italian cities like a new ‘modern skin’, versatile in size, colour and surface finishes of the elements.

The contribution intends to focus on conservation problems of a widespread but still poorly studied heritage and in particular on the difficulty of reproducing the lost covering elements.

The decline of the Italian klinker and lithoceramic industry, until the recent complete closure of the production sector, has in fact generated not only the loss of technical knowledge regarding the laying of the material but also regarding the formulation of the product.

The need to intervene today in a consistent manner on these claddings, which thanks to the excellent performance have not required maintenance for a long time, requires a careful cultural and technical reflection on this ceramic material and at the same time opens a glimmer to the prospect of revitalizing the production of lithoceramics by creating a specific production sector for restoration.

Keywords: Lithoceramics, Cladding, Modern Movement architecture



ABS 392

TECHNOLOGICAL INTERPLAY BETWEEN THE PRECUCUTENI AND CUCUTENI POTTERY FROM EASTERN ROMANIA

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The Precucuteni and Cucuteni cultures occupies the central part of a cultural complex with a large extension in time – more than 1500 years (5050-3500 B.C.) – and space – more than 280 000 sq. km from the eastern part of Transylvania, to the western Ukraine and as far as the Dniepr region. As one of the largest and long-lasting civilization of `Old Europe` can be considered, also, as a foreground for understanding the technological achievements of the South-Eastern Chalcolithic communities.

The aim of this paper is to investigate the relationship between the emergent complexity of the pottery technology registered during the last phases of the Precucuteni and the early phases of the Cucuteni culture. Traditionally, pottery was investigated only with archaeological methods (typology, style and context analysis) and only a few pottery fragments have been subjected to petrographic analysis, at least for the Precucuteni pottery [1].

In order to evaluate the technological characteristics of the ceramic production we engage an interdisciplinary approach to the analysis of pottery samples selected from nine archaeological sites located in eastern Romania. The analytical techniques applied in this study include optical microscopy in thin-section (OM), laser ablation induced coupled plasma mass spectrometry (LA-ICP-MS) for spot chemical analysis of the matrix and temper and X-ray diffraction (XRD) for estimating the mineralogical composition.

By determining the petrographic, chemical and mineralogical characteristics of the pottery samples it was possible to determine the similarities and differences between different groups of pottery determined macroscopically. In addition, the investigation of pottery production process indicated the appearance of increasingly homogeneous products in terms of raw material selection, paste recipes and firing process.

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Keywords: Precucuteni pottery, Cucuteni pottery, Chalcolithic

ABS 365

CONTROVERSIAL CROCKERY

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Several pieces of industrially produced ceramics made ca. 1880 are secreted throughout the display cases of the National Museum of Ireland's Decorative Arts collection. These are mainly intended for domestic use, serving as teapots and plates, cups and saucers, though their surface decoration is incongruent with their functional design. The presentation explores the use of what could be considered controversial imagery and text by referencing the pieces of ceramics telling a highly politicized story in the domestic settings of urban and rural homes in Ireland. It offers a brief consideration of colonial and post-colonial themes in the broader cultural or political context in Ireland, to help frame the discussion of Controversial Crockery in the Decorative Arts Collection of the National Museum of Ireland and beyond. The presentation also examines other ceramic objects within Irish collections that tell multifaceted stories on the technical and aesthetic levels but also on levels relating to politics, history, folklore and material culture.
As a Journal paper this will be published in the Dec. 2018 Museum of Applied Arts (Belgrade).
online journal.

Keywords: Ceramics, Home Rule, Ireland

ABS 936

TOWARDS A FRACTURE MECHANICAL EVALUATION OF THE KNAPPING QUALITY OF STONE TOOL MATERIALS

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The heat treatment of highly silicious rocks, which may structurally be viewed as natural ceramics, to improve tool production by controlled fracturing (stone knapping) is one of the earliest transformative technologies of humankind practiced in several parts of the world. The development of these abilities is certainly an important clue for the cognitive and cultural evolution of anatomically modern humans, because any significant simplification of tool production must have been a great incentive to learn to distinguish proper material types and to control and use firing processes.

In order to understand, for which improvement early humans were inclined to put up with seeking and transporting materials and handle the treatments, it would be most helpful to have a quantitative parameter to qualify a stone tool material in terms of its quality for knapping. Using basic mechanical properties (fracture strength, indentation fracture resistance, elastic modulus and Weibull modulus) of several flint and silcrete samples from a heat treatment study we develop a model to describe the decrease in force needed to knapp a rock by a combination of indentation crack formation and Griffith-type failure in materials with deliberately lowered fracture toughness. The model quantitatively explains the superiority of flint and the simplification of knapping silcrete, providing a tool for further studies comparing all sorts of materials from stone tool findings.

Keywords: Stone tools, mechanical properties, heat treatment

ABS 291

MULTIANALYTICAL STUDY OF GLAZED CERAMICS: TECHNOLOGICAL AND HERITAGE APPLICATIONS

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Objective The multidisciplinary study of the glazed ceramics -both original and replacement pieces- of the Chamberí Metro Station in Madrid (Spain) was performed, in order to increase the knowledge about the raw materials and production technologies used.

Materials & Methods White tiles and pieces with metallic sheen, made up with Spanish clayey materials, were considered. On the one hand, documentary references and ceramic makers were consulted. The original pieces were manufactured in Castellón and Sevilla with local clays, and the replacement ones were made in Madrid with raw materials mainly from Barcelona and Teruel. On the other, a multi-analytical study was followed, by means of X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Polarizing Optical Microscopy (POM) and Scanning Electron Microscopy with Microanalysis of Energy Dispersive X-Ray Spectroscopy (SEM-EDS).

Results The original white tiles were made with very calcareous clays fired at around 950 °C and coated with lead alkali-glazes. The pieces with metallic sheen were manufactured with calcareous and illitic clays fired at temperatures of between 850-950 °C and treated with transparent lead glazes. The replacement pieces had the same appearance as the original but were more resistant. The white ones were made out of quartz-rich, illite-kaolinite and calcareous clays fired at temperatures of >950 °C with an alkali-glaze very rich in zircon and aluminium. The pieces with sheen were made with illite-kaolinite clays very rich in aluminium, with a highly refractory grog addition, were fired at <850 °C and were covered with an aluminium-rich lead-potassium glaze.

Conclusions The multidisciplinary approach carried out has enabled to find out more about the processes involved in the manufacture of these attractive glazed ceramics, which were specially manufactured using Spanish raw materials and very specific technologies. The knowledge acquired will be useful for the conservation and appreciation of glazed ceramics that entail a very characteristic decorative feature of the architecture of Madrid (Spain) in the early 20th century. Moreover, such glazed ceramics are located at an exceptional site, as Chamberí Metro station is the only one in Madrid that have been conserved almost intact its original state and that in the year 2019 celebrates its centenary.

Keywords: Spanish clayey materials, Refractory grog, Metallic sheen

ABS 203

THE GLAZED POTTERY “TIPO SARSINA”: A PARTICULAR LATE-ROMAN POTTERY PRODUCTION

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The glazed pottery “tipo Sarsina” is an exclusive production of Sarsina (FC), a small town situated on the Apennines of Romagna.

This particular glazed production, the only one dated at the beginning of the III century A.D., displays some quite peculiar features.

All the pots are fine and large trays (some of them having even diameter of cm 70), adorned with luxurious decorations, made with moulds.

The motifs are verious: some of them are inspired by vegetal and floral ornaments, others are connected with the mythology or the dionysiac universe.

It is certain that the favourite model of this production was the metal crockery, but the most important comparison is with an important red slip production, the late-roman terra sigillata, that is spread all around the Adriatic area.

The most peculiar characteristic of this particular production is how it was made. Unlike the previous glazed productions, made with a double firing in the kiln (one for the greenware, the other for the glaze), the pots of Sarsina had been fired only once, with greenware and glaze at the same time.

This technique, used normally in the Middle Age, is unusual and inappropriate to make these luxurious trays: in fact the single step in the kiln has caused copious and evident blemishes on the surfaces of the glazes (bubbles, craquelé, detachment or absorption of the glaze). This is because greenware and glaze requires different backing temperatures.

Therefore, the most important question about this interesting and precious production is: “why potters of ancient Sarsina decided to use this technique, although completely unsuitable for those pots?”

Probably this production is an experiment and potters, not well accustomed with this kind of technique, did not know the correct procedure for glazed pottery production, therefore they decided to use the terra sigillata medioadriatica productive phases, to which they were familiar with.

Keywords: glazed pottery, Sarsina, Single firing glazed pottery

ABS 177

ON-SITE PORTABLE X-RAY FLUORESCENCE ANALYSIS OF IZNIK TILES AT EDIRNE AND IN THE EXCAVATION SITE OF IZNIK KILNS

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The production of the tiles in Ottoman Empire had begun as a continued workshop of Seldjuk ceramic art, and after this initial phase, its own technology was introduced into Ottoman art by local craftsmen. Iznik tiles are among the most appreciated pottery masterpieces, and wall decoration in tiles is a significant asset of Unesco World Heritage Edirne mosques [1]. However, the excavations in Iznik, which aim to present the history and cultural heritage of the city, had started in 1969 in the sites of Orhan Imaret and its Bath (Turkish Hamam) and continued for kilns [2].

In this study, we present here the first on-site, non-invasive pXRF (portable X-ray fluorescence) measurements of the glaze, colouring agents and bodies at Edirne and Iznik to understand the change of the technology from earlier periods to the classical period of “Iznik” production. In Edirne, about forty tiles of five mosques have been analysed, while in Iznik, twenty-three glazed and two unglazed shards were studied. Different glazing technologies are evidenced where tin content in the glaze diminishes by centuries. With this study, bismuth is recognized as a representative impurity element which can discriminate different production groups. Body analyses were only carried out on the shards of Iznik tile kilns excavations because the tiles of the mosques at Edirne were mounted on the walls. The decors, which were investigated in this study were blue, turquoise, green, red colours, and black lines. Different cobalt ores have been used (with characteristic As, Cu, Ni, Mn and Bi content) in the blue decors.

This preliminary study on the tiles, which have been excavated at Iznik kiln site and mounted on the walls of mosques in Edirne, shows the efficiency of the pXRF instrument. When compared to the previous measurements carried out with SEM-EDS at the laboratory, the portable system has an equivalent detection capability in discriminating different groups of the tiles regarding their body, glaze and decor compositions.

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Keywords: Iznik, Tiles, pXRF

ABS 852

BLUE PRINT MONOGRAPHIC PROGRAMME: CHARACTERIZATION OF ANCIENT CHINESE CERAMICS

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Blue Print is an international, monographic programme leaded by ASET Stiftung (Berlin, Germany). The prime objective is to conduct studies with an interdisciplinary approach on the origin, the development, the diffusion and the transmission of the knowledge and the technology of high-fired ceramics within and across Eurafrasia. While the main focus of the current scholarship rests largely on the origin and the use of underglaze cobalt blue, the manufacturing techniques, the provenance of the raw materials, the chronology and dating, the authentication, the cultural exchange and the trade contacts [1-6], it overlooks the extraordinary history of a progressive evolution, the long-standing technological development of high-fired ceramics or ‘proto porcelain’, dating back as early as to the 2nd millennium BC.

This paper includes the characterization of 19 shards (proto-porcelains & porcelains) with large-scale, laboratory instruments, e.g., XRD, XRF, Raman Spectroscopy and SEM-EDS. In addition, a portable XRF (pXRF) instrument has been used non-invasively to compare the results obtained by the laboratory equipments. The shards studied in this project are mainly classified in five groups: Jian, Jun, Shufu, Yuan Qinghua and Ming Qinghua. The groups contain polychromic and monochromic glazes, as well as blue and white under-glaze decorated wares.

According to the analyses carried out, the chemical composition, the minerals found on the body and glaze, and the pigments were identified. XRD measurements show mainly the presence of quartz, mullite, calcite and feldspars in the bodies and colouring agents containing cadmium, selenium, iron, cobalt, manganese, nickel, copper in the decors. Raman analysis also confirm the presence of these minerals and pigments found in the decors. The variation of cobalt, manganese, iron, copper, and zinc in the blue areas is consistent with the change of the composition depending on the period of production, from Yuan to late Ming periods. While SEM analysis with the backscatter imaging on the cross section of the shards reveals the body and glaze morphology, EDS analysis shows the major and minor element compositions with the confirmation of XRF analysis.

To conclude, with this project, a research protocol may be created to certificate on-site special collections of Chinese ceramics with non-invasive techniques (pXRF, portable Raman, FORS) in addition to their visual examination.

Keywords: Blue print, Chinese ceramics, Characterization

ABS 83

CERAMICS PUBLIC ART: A SCULPTURE IN THE FACTORY PRODUCTION ENVIRONMENT, THE NEW PARADIGMS OF UNIVERSITY RESEARCH

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This abstact aims to approach new ways of industrial production in ceramics adapted to the demands of projects of monumental sculpture in public spaces.

The Abrigada factory complex, its located 50 km North of Lisbon in the center of Portugal, at the end of the 19th century, a pottery was founded due to the local clay's quality, and introduced the sanitary stoneware production, developing the production of pipes and accessories.
The human and technological heritage, has made possible for sculptors today, to find a suitable environment and technical conditions in which to develop sculpture projects which would never be produced without such unquestionable experience and excellent conditions.
So, the conditions for a partnership with the University of Lisbon were met and it was decided to prioritise research, whether linked to the field of experimentation in the ceramic arts, into technological development, into research into new materials and their impact on the artistic sphere and the market.

In a workshop model resulting from the exchange between institutions, we single out 'Modulos Operandi' held in the Abrigada factory premises. There a group of Fine Arts students met with the aim of carrying out their ceramic sculpture projects from a modular perspective within the framework of factory production. Modulos Operandi provided an opportunity for artistic experimentation in which the technical expertise of the factory workers helped bring the students projects to fruition.

These were undoubtedly the most appropriate and exciting work spaces for the acquisition of technical and artistic knowledge. They constitute examples of institutional investment in long-term partnerships with industry and the local authorities. An investment which, nowadays, has made a definitive contribution to finding technical and artistically innovative solutions, helping to alleviate growing economic difficulties in the ceramics industry, and, it should be said, to remedy technical and scientific shortcomings in university art teaching.

Keywords: monumental sculpture, stoneware industry, technological heritage

ABS 76

APPROACH TO THE EVOLUTION OF THE HUMAN REPRESENTATION IN THE GLASS SCULPTURE

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Even though glass proto-sculptures were produced with deep artistic value since remote glass ages, in the late 19th century the glass sculpture developed, and during the 20th century the Studio Glass Movement reached the maximum level of technical perfection and aesthetic variety. The contribution of the glass knowledge both scientific and technical was essential to attain the appropriate hot and cool procedures for glass working, which allowed the artisans and artists transforming their designs into original creations.
This study focuses on the glass sculpture and the human representation in such material. The historic evolution of the glass sculpture, showing the complete human figure or a part of it, is analyzed from the point of view of their respective production technique and the relationship between the work made on the glass surface (under hot/cool conditions) and the expression of the finished artwork. A set of sculptures and sculptors (among them, Lalique, Sabino, Marinot, Littleton, Libensky, Gómez, García, etc.) are shown as representative examples of the main periods of time in which the glass plays an important role in the sculpture scene. The human representation in the glass sculpture can be considered as a constant throughout the centuries, but it does not constitute the most frequent creative or ornamental motif. Both figurative and abstract human images can be found in glass sculptures, although the figurative ones are majority. This also occurs in sculptures of the contemporary international Studio Glass Movement.

Keywords: Glass, Sculpture, Human representation

POSTER SESSION 1

1- ABS 787

THE EFFECT OF WALL THICKNESS AND PORES SIZE ON THE MECHANICAL PROPERTIES OF HYDROXYAPATITE BASED GYROIDS PRODUCED BY STEREOLITHOGRAPHY

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Ideally, for bone regeneration, bone implant needs highly porous scaffolds, high pores interconnectivity and optimal sizing. These factors allow cells migration leading to an increase of the bone regeneration. Besides these morphological properties, the mechanical properties of the implants need to be comparable to the bone's one and depend on the load applied on this implant, since increasing porosity decreases these mechanical properties, combining high mechanical properties and sufficient porosity can be achieved by generating specific internal design of the implant, moreover, the mechanical properties vary depending on the technique used to manufacture these implants. All classical shaping methods cannot allow enough architectural control of scaffold and pores interconnectivity, while additive manufacturing methods are highly effective in shaping complex objects.

This work concerns the design and evaluation of the influence of macro-porosity and wall thickness on a network phase gyroid structures intended for medical applications as bone implants. this latter represents a structure with a high tortuosity that performs the mechanical properties and controls porosity and interconnectivity which increase the bone osteogenesis.

The aim of this study is to design and introduce gyroid structures with various controlled characteristics, such as pores size and walls thickness into cylinders that would be printed using Hydroxyapatite by direct light processing (DLP) stereolithography (SLA) 3D printing. To study the effect of the different parameters, (pore size, wall thickness) on the mechanical properties of the gyroid structure, three types of specimens would be created:

1. Pores size 400 µm Wall Thickness 200 µm.
2. Pores size 700 µm Wall Thickness 200 µm.
3. Pores size 700 µm Wall Thickness 400 µm.

The mechanical properties of these samples would be then investigated using compression and bending tests. The comparison between the different results would determine the optimal structural compromise between mechanical properties and porosity.

Keywords: Additive Manufacturing, Gyroids, Bone regeneration

2 - ABS 740

HYBRID ADDITIVE/SUBTRACTIVE MANUFACTURING SYSTEM TO PREPARE DENSE AND COMPLICATED CERAMIC PARTS

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As the conventional binder jetting method is still limited in terms of achievable density and finish surface, a new concept of hybrid subtractive/additive manufacturing system has been recently developed. The system relies on a modified binder jetting machine which integrates a slurry-based deposition system and a pulsed laser. The slurry-based deposition system is a spray device which is an alternative to the recoating blade traditionally used to spread layers of coarse powder. By using slurry containing fine ceramic grains, thin layers of highly packed powder can be obtained which is highly beneficial to improve the sintered density of printed parts. The other limitation of binder jetting is the rough finish surface. Thanks to the smallness of the spot size, a pulsed laser is a good option to refine the contour of each printed layers thus enhancing the overall part resolution and smoothness.

The present work exhibits some preliminary results obtained using this new concept of hybrid machine. Parts made in alumina are shown demonstrating the advantages and current limitations of the approach. Densities and geometry of sintered samples obtained using conventional binder jetting, post-impregnated samples prior sintering and the spray system of the hybrid system are compared. First results of parts refining using the laser are also highlighted.

Acknowledgment: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 764935.

Keywords: Binder Jetting, Spray Drying, Density

3 - ABS 961

INCREASING SOLIDS CONTENT OF NANOPOWDER SUSPENSIONS AND THE DENSITY OF GREEN BODIES THEREOF

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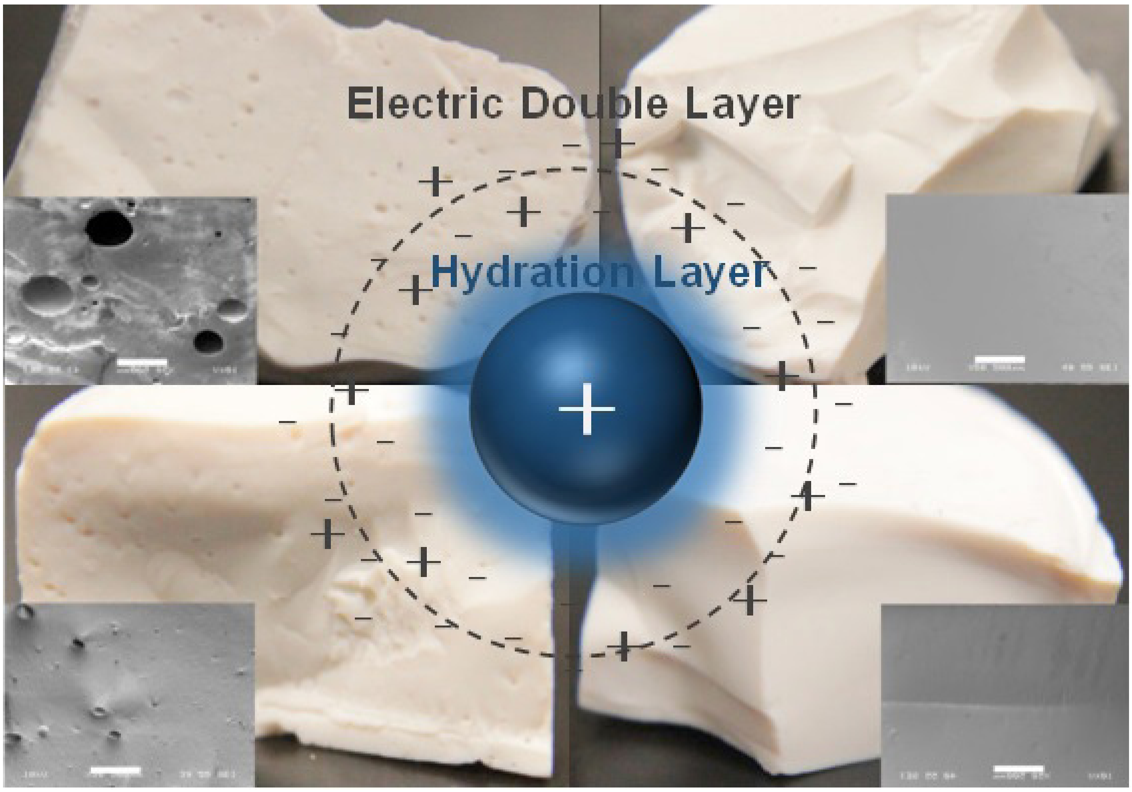
Despite the flexibility offered by a slurry based processing of ceramics their use in production of nano-structured high density bodies is still a challenge. The main limitation of colloidal processing of nanopowders is the unexpectedly high viscosities of their suspensions. These high viscosities restrict the maximum achievable solid content, which, in turn, limit the structural integrity and density of a green body obtained when it is consolidated. Besides, nanopowders tend to agglomerate fast, which creates another challenge to obtain homogeneous distribution of powders in their suspensions and in green bodies. Recently, it has been shown that there exists a hydration layer around oxide nanopowders in addition to the electric double layer formed in their aqueous suspensions. Physical presence of these layers is one reason to obtain extremely high viscosities for nanopowder suspensions because of the high surface area of powders. Therefore, in order to obtain strongly packed, high-density green bodies, the hydration layer should be managed in addition to the electric double layer and the interparticular interactions. In this presentation, the colloidal structure of nanopowder suspensions will be reviewed. The rheological behavior of highly loaded nanopowder suspensions and the methodology for its control through management of colloidal structure will be discussed. It has been shown that successful formulations lead to reduction in viscosities up to 98% for aqueous suspensions of alumina powders with average particle size of 50 nm. As a result, we could increase the solids loadings of suspensions up to at least 35-40 vol%. It will also be presented that, when these suspensions are slip casted, the green body densities as high as 58% could be obtained. Sintering behavior of green bodies made of alumina nanopowders will also be demonstrated.

Keywords: Rheology, Colloidal Processing, Hydration of oxide nanopowders



4 - ABS 713

ADDITIVE MANUFACTURING AND MICROWAVE SINTERING OF ALUMINA

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The aim of this study is to develop a quick and efficient way to process complex-shaped alumina parts. For this purpose, additive manufacturing based on stereolithography as shaping method and microwave heating as sintering method are coupled.

Stereolithography is built by using layer-by-layer photopolymerization of a photosensitive resin using an UV beam. Ceramic particles and organics species, such as dispersant, are added to the UV-photosensitive acrylic resin. The layers are selectively cured in respect of a Computer Assisted Designed file. When polymerizing, polymer traps ceramic particles to form the green part. As stereolithography is an indirect additive manufacturing technique, green parts must be thermally debinded and sintered. Usually, this second processing step is performed in conventional furnaces and the debinding step is time-consuming. The as-sintered alumina ceramics present high-density with mechanical properties close to ceramics shaped by conventional techniques. Microwave heating is a quick and efficient way to sinter ceramics, which allows the achievement of a fine microstructure due to short thermal treatment time. Thus, microwave heating usually leads to better mechanical properties compared to conventional sintering.

Focused on combining these techniques, it is proposed to shape alumina by additive manufacturing and sinter by microwave heating the as-shaped samples. In this study, two stereolithography-based apparatus are used to shape alumina. The main difference between the two apparatus comes from the flow of the slurries in the vat. One has a free flow of the slurry and allows a fine range of coarse alumina; where the second has a tape-casting-like transport band for the slurry and uses a fine-range of fine alumina. Microwave debinding and sintering is performed on the samples shaped by additive manufacturing in a monomode cavity.

The obtained samples are compared with uniaxially-pressed alumina conventionally and microwave sintered samples. A first comparison is made between conventionally-shaped samples and stereolithography-shaped samples. A second comparison is made between the two sintering routes on stereolithography-shaped samples. Comparisons are based on relative densities, mechanical properties, and microstructures. Relative density up to 93 % and Vickers hardness mean value of 11 GPa, can be reached by coupling the methods.

Keywords: Stereolithography, Microwave sintering, Alumina

5 - ABS 598

DEVELOPMENT OF BIO-CERAMIC RESIN-BASED SLURRY IN ORDER TO MANUFACTURE DENSE CERAMIC PARTS WITH THE STEREOLITHOGRAPHY PROCESS

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The additive manufacturing is a technology that has been growing in the past few years. Nevertheless most of the work has been done on polymers and metals at the expense of ceramic materials. Therefore, some research is still to be done in this field. The stereolithography is an additive manufacturing technique that enables to have one of the best resolutions. However, considering the ceramic materials, it is still difficult to print dense parts using the stereolithography because cracks and defects appear during the debinding and sintering steps.

Thus, the purpose of this work is to present some ideas and first results on the optimisation of the stereolithography process of bio-ceramic materials. The stereolithography process being based on the dispersion of ceramic powder into a photopolymer resin, the optimisation of the process goes along with the development of suitable photopolymer resins.

The idea is to develop a new mixture of photopolymers which can present a more suitable thermal degradation pattern in order to facilitate the debinding of the green part. The resin is meant to be used along with bio-ceramic powders: Hydroxyapatite and β-Tricalcium phosphate, in order to print bio-compatible bone implants.

In order to evaluate the suitability of the resin, some curing experiments with an UV light will be done as well as some thermogravimetry analysis. Once the resin will match the expectations some additives, such as dispersant, will be added in order to prepare a ceramic slurry which has to be homogenous and stable. Afterwards, the curing of the slurry will be evaluated to see if the mixture is printable with the stereolithography machine.

The development of a new resin could improve the density of the final ceramic parts, therefore improving the control of their architecture.

Acknowledgment: This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 764935

Keywords: Stereolithography, Bioceramics, Photosentive resin

6 - ABS 578

FACILE PREPARATION AND OIL-WATER SEPARATION OF HYBRID MEMBRANE BASED ON PSMA AND SiO_2 NANO-CERAMIC ADDITIVE

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Nano-silica powders have been successfully applied as an additive in many fields such as modern ceramics, inorganic conductive materials, concrete, organic-inorganic composite membranes due to their excellent physical and chemical properties. In this study, SiO2 nano-ceramic powders were added in functionalized poly (styrene-alt-maleic anhydride) (PSMA) to obtain organic-inorganic hybrid membrane with hydropholic and oleophibic properties. Hydrophilic membranes can be used for gravity-driven oil-water separation, and are more resistant to fouling. In order to improve the dispersibility of the nano-silica powder, a structure with coupling function was introduced into the polymer main chain by radical copolymerization. The PSMA/SiO2 hybrid membranes were prepared on the stainless steel meshes by dip-coating method. The effects of PSMA/SiO2 ratio and the concentration of dip-coating solution on the properties of the oil-water separation were investigated. The structure of the functionalized PSMA and microstructure characterization of the hybrid membranes have been conducted by means of FTIR and SEM, respectively. When the oil-water mixture contacted the modified meshes coated with PSMA/SiO2 hybrid membranes, water droplets could penetrate the mesh quickly while the oil was trapped in the upper part. In this way, the oil-water mixture could be separated effectively, with oil-water separation efficiency exceeding 98 %. This method is a potential candidate in the employment of oil-water separation with antifouling property.

Keywords: Nano- silica, Hybrid Membrane, Oil-water Separation

7 - ABS 471

DEVELOPMENT OF A SUPPORTSUSPENSION FOR THE DIRECT INKJET PRINTING PROCESS

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Over the last years, additive manufacturing gained more and more importance. The reason for this is the possibility to produce complex geometries with lesser material loss and a high precision as well as surface quality. According to the current state of technology one can distinguish between a plurality of manufacturing methods. Stereolithography, selective laser sintering and three-dimensional printing (3DP) are just a few of the possible methods. The additive manufacturing process Direct Inkjet Printing under development at the institute of mineral engineering belongs to the three-dimensional printing process and uses the multi-layer printing of tailor-made suspensions for the production of ceramic structures and components. To ensure dimensional accuracy, the inks must have well-defined rheological properties (viscosity and surface tension). Support structures are necessary to implement complex, undercut or overhanging geometries. These are realized by means of carbon black suspensions.

In the preparation of the water-based carbon black suspensions, it is important to note, that they not only have a sufficiently long-term stability, but also the corresponding rheological properties, which allow a simultaneous printing with ceramic suspensions. For this purpose, experimental studies are carried out, in which the rheological properties and the stability of the suspensions are optimized by the variation (glycerin 85% and ethanol) or addition of additives (NP10; Triton X-100; BYK420, 425 and 4720) and by the usage of various dispersing methods (ultrasonication and mechanical mixing (Ultraturrax)).

From previous experiments, the following initial findings are obtained:

1. Increasing the glycerol content causes an increase in the viscosity whereas lowering the ethanol content causes an increase in the surface tension
2. BYK425 results in a sharp increase in viscosity
3. NP10, Triton X-100 and BYK425 lead to no change of the long-term stability
4. BYK420 and BYK4720 significantly improve long-term stability
5. Dispersing methods do not appear to have any influence on the stability

After all, it is possible to control the rheological properties of the suspensions, bearing in mind that new additives could have an influence on the rheological properties. Furthermore, it was possible to generate long-term stable suspensions, but their rheological properties need to be further optimized in order to generate the desired geometries in the printing process. Therefore, much research is still needed to generate a tailor-made carbon black suspension for direct inkjet printing, which complies all conditions.

Keywords: Support suspension for 3DP

8 - ABS 389

OPTIMIZATION OF LIGHT-ACTIVATED RESINS FOR ADDITIVE MANUFACTURING OF ZIRCONIA

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Digital Light Processing (DLP) is an Additive Manufacturing (AM) technique that utilizes light to selectively cross-link a photoactivated resin in a layer by layer fashion to build a free-standing object. The light comes from a projector, equipped with a high pressure mercury lamp. Each layer is exposed all-at-once with a selectively masked light source. Because the whole layer of the structure is produced in one exposure step, the build time is considerably shorter than other AM techniques. Moreover, with this process a high level of accuracy and surface smoothness is achievable. The DLP process has an increasing relevance also outside polymeric area, promoting the manufacturing of ceramic structures with complicated morphology, high resolution and good surface quality.

In this work, commercially available photo-curable polymers are filled with 3Y-TZP zirconia powder. For printing ceramics, the photosensitive resin is typically filled up to 30–50 vol% of ceramic particles. Ceramic powder addition results in a drastic increase of viscosity of the slurry, compared to the resins. Besides, zirconia powder induces an important light scattering on the particles' surface, and hence the increase of the reflectance of the slurry. As direct consequence, the light penetration in the slurry during the DLP process is hampered, therefore a longer exposure time is necessary to get the suitable cure depth and obtain printed components. An unwelcome border effect, with distortions of the dimension in final geometry, is strictly connected to a longer exposure time, and hence to the increase of the build time of components. These technological issues can be reduced by the optimization of the ceramic-resin slurry.

The most common radical photoinitiators for acrylic resins are based on phosphine oxides which react upon exposition to the 405 nm line of the mercury lamp. Spectrophotometric studies highlighted that a layer of zirconia-resin slurry has transmittance close to zero at such wavelength, while the transmitted light progressively increases at wavelength longer than 550 nm. The photo-curing performance of the resin can be enhanced in two ways: adding a photosensitizer for the radical photoinitiator which absorbs the transmitted red component of the incident radiation, and also differentiating the type of radical photoinitiators to increase the photoreactivity.

This work deals with the most common problems related to AM of ceramics using the DLP technique, providing some basic solutions for the tailoring of already available photocurable resins loaded with ceramic powders.

Keywords: AM, DLP, Zirconia

9 - ABS 317

INFLUENCE OF PRINTING PARAMETERS ON PROPERTIES OF ALUMINA CERAMICS PREPARED BY FUSED FILAMENT FABRICATION

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Alumina 3D objects prepared by fused filament fabrication method were investigated in terms of their printability and physical properties. A filament with diameter of 1.75 mm containing 50 vol. % of commercial alumina powder with particle size of 0.4 – 0.7 µm was used for manufacturing of green bodies in a form of cylinders with diameter of 12 mm and height 4 mm. Printing variables such as infill amount and layer height affected significantly shrinkage, bulk density and porosity of sintered alumina ceramics. Using properly optimized printing parameters and debinding cycle, it was possible to prepare nondeformed ceramic objects. In order to obtain green bodies without visible defects or overflows it was necessary to find appropriate rectilinear infill for each layer height. Results showed that with the infill levels higher than 65 % and the single layer height lower than 0.3 mm only relative density around 74 % after sintering at 1400°C for 1h can be obtained. As a future outlook, used high purity alumina filament could be applied in preparation of relatively small products of complicated design, however the debinding process has to be optimized.

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Keywords: Alumina, 3D Printing, Fused Filament Fabrication

10 - ABS 286

SHAPING OF COMPLEX ALUMINA COMPONENTS VIA LASER ADDITIVE MANUFACTURING OF SPRAY-DRIED CERAMIC GRANULES

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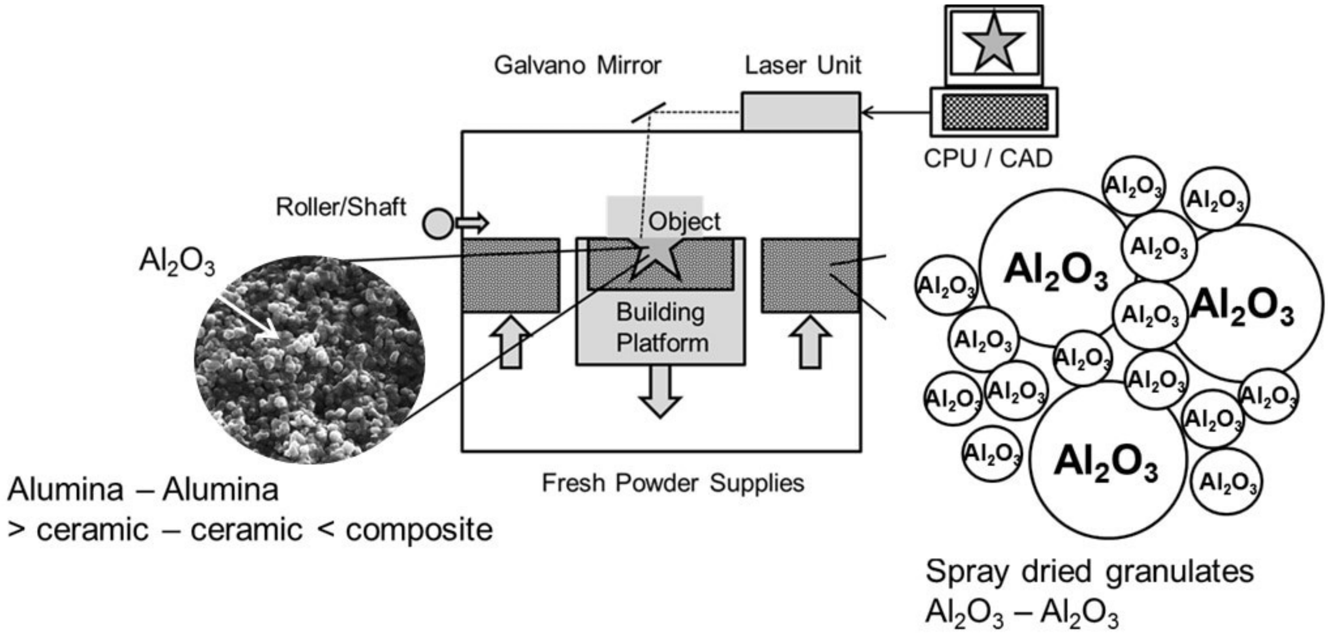
Shaping of complex parts with high precision and high strength of the workpiece is a key challenge in ceramics processing. This is in combination with long processing time and cost-intensive post processing a major obstacle for a broader application of high tech ceramic parts. Selective direct laser sintering and melting (SLS/SLM) could be a solution to these problems. Being an emerging technology in metals and polymers, problems like crack formation and weak densification have to be still approached for the production of high performance ceramics.

The absence of understanding the interaction of laser light sources with the ceramics based materials and the slow sintering kinetics of ceramics is today the cause of no existing direct SLS process available to consolidate ceramic powders to dense structures with convenient material properties.

Based on our approach the starting ceramic powders are granulated by spray drying to achieve a high flowability and powder bed density for solid and liquid phase sintering and failure free densification. The variation of the composition and morphology of these doped nanocomposite granules affects the absorption behaviour to the laser light. The focus here is on the optimization of particle size, raw powders and additives to improve the interaction between the laser and the granules. Reduction of thermal stresses and cracks formation during laser-processing is also a challenge to be solved in the ongoing work.

Keywords: SLS/SLM of alumina, Spray granulation, nano powder dispersing



11 - ABS 258

DEVELOPMENT OF COMPOSITE FILAMENTS FOR FUSED DEPOSITION MODELING OF OXIDE CERAMICS

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The difficulties in the preparation of highly filled composite feedstock in the form of spooled filaments however still constrain the fused deposition modeling (FDM) technology for manufacturing of ceramics. This study was focused on the challenges of creating and characterization of thermoplastic ceramic filaments for products made using 3D-printing. The inorganic fraction used for preparation of filaments mostly consists of aluminium and silicium oxide components. Capillary rheometry was used for analysis of apparent viscosity (resistance to flow) over a broad range of shear rates with respect on filling grade of ceramic part at given temperature, which is comparable to the conditions encountered in extrusion process. Additionally, strength of composite filaments and the homogenity of dispersed ceramic particles in thermoplastic matrix by scanning electron microscopy were investigated for individual filaments in order to obtain complex information needed for production of filaments suitable for fused deposition of ceramics (FDC). From the selected filament a green body of demonstrator was printed and sintered. The software parameters of the 3D-printing were modified to determine their effect on the properties of green bodies prepared.

Acknowledgement The financial support of the Slovak Grant Agency for Science VEGA grant No. 1/0906/17 and Slovak Research and Development Agency APVV-16-0341 are greatly appreciated. This work is also based on the results of the project Center for Applied Research of New Materials and Technology Transfer, ITMS 26240220088, supported by the Science and Research Operational Program by the European Regional Development Fund.

Keywords: Fused Deposition of Ceramic, Composite Materials,3D-Printing

12 - ABS 239

PREPARATION OF $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-d}$-$Ce_{0.85}Gd_{0.15}O_{2-d}$ ALL-CERAMIC COMPOSITE MEMBRANES BY 3D-PRINTING TECHNIQUE

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Objective BaCe0.65Zr0.20Y0.15O3-δ-Ce0.85Gd0.15O2-δ (BCZ20Y15-GDC15) dual-phase material is currently one of the most studied composite as a promising dense ceramic membrane for H2 separation and purification at T > 600 °C. [1-3] However, the optimization of the membrane architecture represents one of the most important issues to be solved for their practical applications. The asymmetric configuration, consisting of dense films supported on porous substrates, is considered a good promising strategy to improve the hydrogen permeability of these systems. Though, only few attempts are reported in the literature for the preparation of these membranes in asymmetric configuration. [4]
The purpose of this study was to evaluate the preparation of asymmetric membranes based on BCZ20Y15-GDC15 composite by 3D-printing technique.

Materials and methods BCZ20Y15 powders were supplied by Marion Technology (France). GDC15 and BCZ20Y15-GDC15 powders were prepared as described elsewhere [1]. The slurries for 3D-printing were prepared by ball-milling by mixing BCZ20Y15 and GDC15 powders with the desired amounts of solvent, binder and plasticizer. For the preparation of porous a suitable amount of pore former was also added. The rheological behaviour of the most promising slurries were characterized by means of absolute rheometers and rheometers for high shear rates. As printed substrates having diameter of 20 mm and thickness of 1 mm were prepared by a self-assembled 3D-printer.

Results The results shown that the technique is effective for the production at laboratory scale of BCZ20Y15-GDC15 all-ceramic composite samples. The optimal set of both the rheological and printer parameters is critical for obtaining as printed cylinders with the correct size and without defects. Viscosities above the 40-50 mPa.s and a shear thinning behaviour are necessary to avoid deformations of the cylinder under its own weight. Alcoholic solvents seem the most performant due to their high evaporation rate. Moreover, the heated bed helps to solvent evaporation and the shape maintaining.

Conclusions As printed asymmetric membranes based on BCZ20Y15-GDC15 all-ceramic composite were successfully prepared by the effective and low cost 3D technique. High attention must put on the rheological and printing parameters.

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[4] E. Mercadelli Et al., Ceram. Int. 43 (2017) 8010.

Keywords: All-Ceramic Composites, 3D-Printing, Hydrogen Separation

13 - ABS 212

THREE DIMENSIONAL PRINTING OF PHOTOCATALYTIC TITANIUM DIOXIDE-BASED FILTERS

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Energy and environmental issues are among the most dramatic and urgent challenges that modern society has to face. Researchers are therefore spending a lot of efforts on more eco-friendly alternative technologies for many daily life areas. Among them, sustainable energy production and pollutant removal are two of the areas in which intense research is being carried out. Titanium dioxide (TiO_2)-based photocatalytic filters for water purification was produced by Fused Deposition Modelling (FDM) using polylactic acid (PLA) from renewable biomass resources as the thermoplastic matrix. This environmental friendly approach allows shaping complex composite filters by immobilizing photoactive TiO_2 nanoparticles (NPs) in a biopolymer. The optimization of the colloidal dispersion and stabilization of the inorganic NPs in the PLA solution were obtained by a careful surface modification of TiO_2 NPs with branched polyethylenimine (PEI). This allows the homogeneous distribution of nano-photoactive sites in the TiO_2/PLA FDM filaments and therefore into the 3D filters. The proposed new route of processing, recently patented (ES1641.1356), improves the dispersion of nano-charges comparing with the traditional thermo-pressing routes used for mixing thermoplastics based composites, avoiding the thermal polymer degradation and providing a customized product. In this work, the evolution of methyl orange (MO) degradation under sunlight is studied considering both the TiO_2 content in the composite filters and their geometries. Filters with a TiO_2 NPs content up to 30 wt.%, 20 mm of diameter and 40% of infill (F7, Figure 1) exhibit a 100% MO degradation after 24 h of light exposition due to the extremely uniform dispersion of the nanopowder within the polymer matrix in the FDM feedstock. Moreover, the augmented inorganic charge in the polymer matrix, as well as the scaling up of the printing parameters employed produce a valuable wall roughness/porosity in the filter rods that propitiates the photoactivity.

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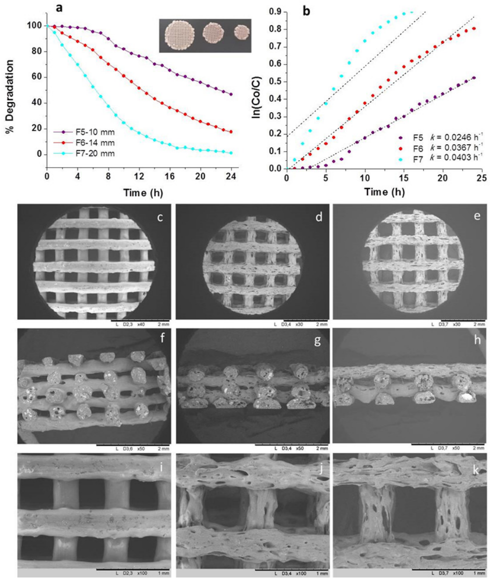
Keywords: Fused Deposition Modelling, Colloidal Processing,Photocatalytic filter



14 - ABS 97

ABSORBANCE ENHANCERS OF CERAMIC POWDERS FOR SELECTIVE LASER SINTERING

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Objective This is a preliminary survey to validate a ceramic powder/dopant composite before using it in a Selective Laser Sintering/Melting machine. As oxides are known as almost non-absorbent to fiber lasers energy, this study aims to verify possible alternatives to enhance energy absorption of ceramic powders when exposed to a fiber laser. The objective is to reach around 60 % of energy absorption corresponding to the minimum amount of dopant possible, the first step to allow a ceramic power to be manufactured by Selective Laser Sintering/Melting. The importance of parameters like dopant/powder proportion, interaction during sintering and morphology are investigated.

Materials & Methods The ceramic powder used is 8% Yttrium Stabilized Zirconia (8YSZ - Marion Technologies, Verniolle) and the alternative absorption enhancers dopants are SiC (Marion Technologies, Verniolle), TiC (Marion Technologies, Verniolle), Carbon Black (Alfa Aesar, Karlsruhe) and Graphite (Alfa Aesar, Karlsruhe), with the respective particle sizes (d50): 27, 0.55, 0.85, 1.7 and 8 µm. Eight samples were prepared with the chosen proportions of 0,25 wt.% and 0,75 wt.% of each dopant and mixed uniformly to the 8YSZ with a mortar. Absorbance was measured using a Perkin Elmer UV/Visible/NIR spectrometer at CIRIMAT/INP, Toulouse. To simulate the exposure to a Nd:YAG fiber laser ($\lambda = 1065$ nm), the absorption of each sample was measured at this same wavelength. The best absorption case is pressed and sampled to be sintered in order to investigate the powder/dopant interaction using the selected proportion. Pressed pastilles were prepared with 2 wt.% binder and sintered at 1200° C during 4 hours.

Results The highest absorption/amount ratios were obtained with 8YSZ/0,75 wt.% TiC, 8YSZ/0,75 wt.% Carbon Black, 8YSZ/0,25 wt.% TiC and 8YSZ/0,25 wt.% Carbon Black, enhancing the absorbance from 4% of pure 8YSZ to around 68%, 67%, 58% and 55%, respectively. Comparisons with literature show that the particle size has an important role during absorption. The powder containing 0,25 wt.% TiC was selected by the best rapport amount/absorption to be pressed as pellets and sintered to confirm their compatibility during thermal treatments. Further investigations must be done to confirm that all TiC transformed to TiO2 during sintering.

Conclusions Additive manufacturing of pure ceramics is a great challenge, however, the use of a small amount of absorption enhancers may allow its production with Selective Laser Sintering/Melting. This study has validated the use of TiC as dopant to enhance the absorbance to Nd:YAG lasers. Also, the feasibility of using 0,25 wt. % TiC with 8YSZ during sintering was positive. This selected sample must be tested in a Selective Laser Sintering/Melting machine as next step of this work.

Keywords: Yttrium Stabilized Zirconia, Absorbance, Selective Laser Sintering

15 - ABS 85

THERMAL DEBINDING AND SINTERING OF POLYMER-CERAMIC COMPOSITE FILAMENTS FOR FDC

P. VETESKA [1], Z. Hajduchova [1], K. Randova [1], R. Plavec [2], L. Omanikova [2], K. Tomanova [2], J. Feranc [2], L. Baca [1], M. Janek [1,3]

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Fused deposition of ceramics (FDC) is a form of additive manufacturing employing ceramic-polymer composite system in a form of filament as a precursor [1]. Although various other methods for deposition of ceramics by additive manufacturing are used, such as Robocasting (RC) [2], layer-wise slurry deposition [3] and many others, one of the main advantage of using the ceramic-polymer composite in the filament form is the possibility to use commercially available Fused Filament Fabrication (FFF) devices [4].

The aim of this work is to study a the debinding and sintering behaviour of polymer/ceramic composite system suitable for preparation of 3D green bodies by FDC and to optimize the composition and the preparation of the composite material to obtain a material with minimum shape deformation during the debinding and sintering process.

Small composite parts with the dimensions of approx. 40mm have been manufactured using a commercial AM device (Leapfrog 3D Printers, Netherlands). The parts were subsequently processed by thermal debinding and sintered using commercial laboratory furnace (CLASIC CZ Ltd., Czech Republic), obtaining ceramics with shape identical to the original green body. Several thermal debinding regimes have been investigated.

Initial results confirm that the shape deformations are strongly dependent on ceramic filler/polymer matrix ratio. At the same time, when using composite filament with high volume fraction of ceramic filler it was possible to demonstrate the rapid speed up of the debinding process without significant green body and final ceramic deformations.

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Keywords: Fused Deposition of Ceramics, Debinding, Sintering

16 - ABS 630

THERMOELECTRIC PROPERTIES OF Al-DOPED ZnO FABRICATED BY FLASH SINTERING

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The Flash sintering process raised a great interest in the past few years due to its ability to densify ceramic materials in a few seconds, at lower temperature than conventional sintering. The simultaneous application of electric and thermal fields allows an ultrafast densification and consequently a drastic reduction of time and cost of the sintering process.

ZnO-based materials are among the best n-type thermoelectric oxides known to date. In this study, doped ceramics (Zn1-xAlx)O were prepared from ZnO and Al(NO3)3, 9H2O ultrapure powders. We examined the influence of aluminum doping (from 0 to 2% at.) on the Flash sintering threshold conditions in air (furnace temperature and applied electric field). The influence of the current limit on the final relative density was also examined for each composition.

After sintering, densities and microstructures of samples were compared and discussed according to doping level and Flash conditions. Their electrical conductivity and Seebeck coefficient were also investigated from room temperature to 900°C. Data were compared to those obtained for samples densified by conventional and Spark Plasma Sintering (SPS).

Acknowledgement
This study is supported by ERDF and the Walloon Region, in the frame of IMAWA-FLASHSINT research project (program 2014-2020).

Flash Sintering,Thermoelectric,Zinc Oxide

17 - BS 738

COUPLED PHASE DIAGRAM EXPERIMENT AND THERMODYNAMIC ASSESSMENT OF THE Li_2O-ZnO SYSTEM

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Lithia (Li2O)-containing oxide systems are important in glassmaking, ceramic engineering, solid state electrolyte and fuel cell design. ZnO has also attracted attentions for the applications in transparent high-power electronics, UV-light-emitters, piezoelectric transducers, gas sensing and solar cell because of its well-known wide band gap and non-linear optical property. However, the phase equilibria for the Li2O-ZnO system has not been well-determined yet.

In this study, the phase diagram experiments were carried out using classical equilibration and quenching technique and DSC analysis, followed by EPMA and XRD phase analysis. In order to prevent the evaporation and contamination of the samples during the high temperature experiments, a sealed Pt capsule was used for sample crucible. Two stoichiometric intermediate compounds, Li10Zn4O9 and Li6ZnO4 were found to exist as stable solids within this system. Based on the experimental data, thermodynamic assessment was carried out, and new phase diagram of the Li2O-ZnO system is prepared.

Keywords: Li2O - ZnO system,Phase diagram experiment,Thermodynamic assessment

18 - ABS 589

MOLECULAR DYNAMICS SIMULATION OF THE DENSE PACKING OF SiC BIDISPERSE POWDER MIXTURE

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Silicon carbide is widely used in many industries because of the unique combination of physico-mechanical properties. In most cases the manufacture of bulk products of this ceramic material occurs on basis of a micropowder mixture by pressing or injection molding. To obtain a material with a density close to monocrystalline the initial charge must have the maximum possible packing density of particles. For this reason, mixtures of two or more fractions of particles are commonly used. In this paper, the determination of the optimal ratio of fractions, which provides the greatest degree of particle packing, is carried out by the method of numerical simulation.

Numerical simulation of dense particle packing is based on the molecular dynamics method. A model potential of the interaction of particles of the "hard core" type, which ensures faster convergence of the calculations, is introduced. The generation of the initial position of particles and their sizes according to size distribution function occurs with the help of a random number generator. The result of the calculations is a stationary position of all particles, characterized by a minimum free energy and without mutual intersections. In this study, a region of size (200 × 200 × 200 μm^3) is considered, which is filled with particles of two fractions. The particle sizes of each fraction are described by given distributions obtained for real commercially available grades of SiC powder (F240 and F1200). The average number of particles involved in each version of a numerical experiment was about 200,000. An important feature of the method is its fast convergence with dense packing of particles.

More than 70 thousand hours of CPU time were spent on the calculations, which is due to the need to collect statistics. It is shown that the densest packing (82%) is obtained with a volume ratio of large (F240) and small (F1200) fractions of 83 and 17%, respectively. The simulation results are verified experimentally for the slip casting method. Thanks to this selection of the ratio of SiC powder fractions in the mixture, Si/SiC ceramics with a density of 3.13 g/cm^3 (97% of monocrystalline) and with a good combination of strength (E ~ 450 MPa) and thermal ($\lambda \sim 200$ W/(m K)) properties were obtained.

This work was supported by the King Abdulaziz City for Science and Technology (Saudi Arabia).

Keywords: Silicon Carbide Ceramics, Dense Packing, Molecular Dynamics Simulation

19 - ABS 565

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF THE EFFECT OF SUSCEPTOR ARRANGEMENT DURING SINGLE-MODE MICROWAVE SINTERING

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Objectives Testing the relevance of finite element simulation to control susceptor-assisted microwave sintering.

Materials & Methods Sintering tests were carried out on TiO2 compacted powder inside a 915 MHz single-mode cavity. Two SiC plates, set on both sides of the compact and parallel to the electric field, acted as susceptors (see Figure 1).

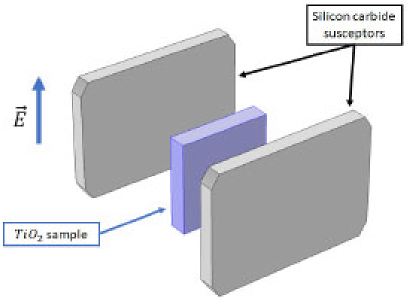

Figure 1: Element arrangement

Microwave sintering finite element simulations,including electromagnetic, thermal and mechanical coupling, were carried out with COMSOL Multiphysics® 5.3 software. Sintering deformation was described with a rough sintering model fitted from dilatometric tests.

Results Two configurations have been tested: in the first one, the sample and the SiC plates were perpendicular to the electromagnetic wave propagation (aka Configuration 1) and in the second one the sample and the SiC plates were parallel to the electromagnetic wave propagation (aka Configuration 2). Whereas in Configuration 2, the TiO2 shrinkage was homogenous, in Configuration 1, the sample tended to bend, evidencing the non-uniformity of shrinkage.
Numerical simulations showed that the two configurations result in very different heating processes. In Configuration 1, indirect heating occurs: the susceptors screen most of the electromagnetic field, so that the fraction of power dissipated in the compact is negligible. Concerning Configuration 2, the simulation revealed that the heating mode is similar to Conguration 1 at low temperature, while the heating gets hybrid at high temperature, as the dissipated power increases in the compact, due to TiO2 dielectric losses increasing.
The difference in heating mode leads to different temperature distributions in the compact. In Configuration 1, the susceptor in front of the microwave generator catches a higher part of the electromagnetic power and reaches higher temperatures than the other one. This results in a very heterogeneous heating of the compact, which then exhibits a non-uniform deformation. In Configuration 2, the temperature is much more homogeneous, as it is usual in hybrid mode.

Conclusion Numerical simulation proved to be efficient for a better understanding of susceptor-assisted microwave sintering. It is a helpful guide for designing susceptor configurations in the microwave cavity with a view to get uniform heating.

Keywords: Microwave sintering, Hybrid heating simulation, Temperature homogeneity

20 -ABS 552

THEORETICAL ESTIMATION OF COMPOSITION OF AMORPHOUS PHASE IN THE PRECURSORS FOR ALKALI ACTIVATED SYNTHESIS

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Alkali activated materials present potential replacement for cements, mortar and ceramics due to lower energy consumption during production process, no need for raw materials, waste consumption and no additional waste production, possibility to immobilize toxic and radioactive waste etc. [1]. During alkali activated synthesis of waste material with alkali and/or alkali glass formation of matrix takes place. Matrix is made of SiO4 and AlO4 tetrahedrons joined by oxygen bridges. Al in tetrahedrons in the matrix is in coordination number 4 instead of its natural 3. Therefore addition of cations from 1st group is needed to compensate this “non-stable state” of Al. Suitable precursors have to have enough Si and Al in amorphous form, which is the most important criterion used to evaluate waste material’s potential for alkali activated synthesis. This can be assessed by performing chemical (XRF) and mineralogical (XRD) analysis from which is then calculated the mass percentages of amorphous elements from 1st and 2nd group as well as for Si and Al.

XRF and XRD results are used to theoretically estimate needed amount of additives and to estimate which additives might be preferred according to the prechosen ratio of the elements in the mixture for alkali activated material. Several approximations were made during calculation depending whether precursor was mostly amorphous materials (such as mineral wools) or partially crystalline. Rietveld refinement was further applied on alkali activated material to evaluate the theoretical model. Proposed theoretical calculation was used in experimental work, where it has proven its usefulness on several different waste materials: fly ash, bottom ash, raw material for ceramics, waste foundry sand, rock wool, slag and refractory material.

ACKNOWLEDGMENTS
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Keywords: XRF and XRD, amorphous phase, alkali activated synthesis

21 - ABS 550

FINITE ELEMENT MODELING: A FIRST STEP TOWARD THE STUDY OF COUPLING BETWEEN PYROELECTRIC AND AND SOFT FERROMAGNETIC BASED EXTRINSIC MULTIFERROICS

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Multiferroic are materials, simultaneously exhibiting several ferroic properties in a single phase typically, ferromagnetism (a magnetisation that is switchable by an applied magnetic field) and ferroelectricity (an electric polarisation that is switchable by an applied electric field). Rapidly, this class of materials was extended to multiphasic systems, leading to a so called extrinsic multiferroism including nanomagnets and ferroelectics coupled thanks to their ferroelasticity (a deformation that is switchable by an applied stress). These systems are commonly composed of magnetostrictive and piezoelectric nanomaterials. They have drawn attention for use in ac or dc current sensors, energy harvesters, and other multi-functional devices, owing to their strong magnetolestic coupling.

In this work we propose to build a new kind of extrinsic multifferoics, using the temperature instead of mechanical strains as a coupling vector between the ferromagnetic and their ferroelectric components. In this case, the former is chosen as a soft ferromagnet able to heat under an ac magnetic field while the later is a pyroelectric able to generate current under a temperature change.

The investigation on such thermo-magnetoelectric systems requires the development of numerical and analytical methods that combine the thermic and electromagnetism governing physics equations. As a pioneer research we present in this work the result of modeling performed on a 0-3 type and artificial multiferroic using a multiphysic code based on the finite element method, with a special emphasis on the variability of the magneto-pyrroelectric coupling coefficient when a random dissemination of soft magnetic nanoparticles is applied to a pyrroelectric matrix.

Keywords: Magnetoelectricity, Pyrtoelectricity, Modeling

22 - ABS 502

THEORETICAL ANALYSIS OF DENSIFICATION KINETICS IN FINAL SINTERING STAGE OF NANO-SIZED ZIRCONIA

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The densification behavior of powder compacts can be characterized by determining the activation energy, grain-size exponent and unspecified density function. Several methods have been proposed to determine the activation energy and the grain-size exponent, but no method for the density function. In this study, a method is proposed to determine the unspecified density function during isothermal sintering of nano-sized Y_2O_3-stabilized zirconia powder, and the existing sintering models are evaluated from the experimentally determined density function.
Densification and grain growth are examined during isothermal sintering of nano-sized 8 mol% Y_2O_3-stabilized zirconia powder.
By taking concurrent grain growth into account, a possible value of the grain-size exponent n was examined. The Coble's corner-pore model recognized widely for the final stage was found not to be applicable for explaining the densification kinetics. The corner-pore model of $n=4$ shows a significant divergence in the kinetics at different temperatures. Microstructural observation shows that most pores have a size comparable to the surrounding grains. The observed pore structure is similar to the diffusive model where single pore is surrounded by dense body. The diffusive model combined with theoretical sintering stress predicts $n=1$ or $n=2$, which shows a good consistence to the measured densification kinetics.
It is found that the widely recognized Coble model is not applicable for explaining the experimental densification kinetics in the final sintering stage. The reason is that the pore structure during sintering of nano-sized powder is quite different from the Coble's corner-pore model. We show that the diffusive model which pore structure is similar to the actual pores can explain the observed densification kinetics. We emphasize a necessity of new sintering model for nano-sized powder. During sintering of nano-sized powder, it is found that the densification kinetics can be explained distinctively by the diffusive single-pore model.

Keywords: Densification, Grain growth, Sintering model

23 - ABS 477

FAILURE STRESS ENERGY FORMULA

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In the process of exploitation of ceramic materials and ceramic composites often we encounter not only high mechanical stresses but also thermal loads and air-thermal shocks. Thus for example on power transmission lines, in the process of starting and operation of water and air turbines, high power loads come on turbine discs and wings. These loads are transformed into failure/rupture stress energy, when strength of work-pieces is less than loads. Micro-cracks are in all materials and there can also be cracks created as a result of technological failures, on the ends of which at critical loads, maximum stresses use to develop, high energies are developed and plucked from the crack top, resulting in destruction of objects. Considering such extreme operation conditions computation of energies which contribute to materials catastrophe seems rather interesting

Taking into consideration terms of exploitation of materials in industry, we studied their exploitation properties by modern research methods. The formula parameters were selected on the basis of study and generalization of micro- and macro-structural, micro- and macro-mechanical characteristics of ceramic materials

The formula covers the process of creation of energies as a result of mechanical and thermal loads affecting the work-piece and analyses of mechanisms of impact of these energies on the cracks existing in the material; results of energies affecting the existing cracks as a result of such loads and results of starting of mechanisms of spreading of energies developed inside the work piece, which lead material to the catastrophe

On the basis of crack development mechanism the universal relationship of total energy of the workpiece and its mass was established, considering crack developing speed under critical stress conditions. Failure stress energy formula has been offered.

Keywords: Crack, Development, Speed

24 - ABS 430

INFLUENCE OF COMPOSITION CHANGES ON VISCOELASTIC PROPERTIES OF CLAY-CEMENT BINDERS

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Clay-cement sealing binders are used in many areas especially in the construction and renovation of flood protection. Modernization of flood embankments, often located in inaccessible area, requires the transport of finished binder over considerable distances. The most common solution is to create a portable base in which the binder is produced in the form of a suspension, and then it is transported using pipelines to the place of work. The viscoelastic properties in the liquid state belong to the main criteria for their usefulness (i.e. the possibility of submerging to the ground and expected crosslinking afterwards).

This work presents the results of studies concerning freshly prepared clay-cement binders based on Belchatow polymineral clay and KOC kaolin, Portland Cement and Calcium Aluminate Cement with the addition of water glass as the initiator of the hydration reaction. The flow curves, values of elastic modulus G', loss modulus G'' and time of the 'crossover' phenomenon were compared. The influence of composition changes on viscoelastic properties of liquid state binders in the aspect of functional properties was determined.

These studies confirmed that viscoelastic properties of clay – cement binders depend on type of clay minerals and type of cement. In case of their application, measurements of viscosity and elasticity modulus should be carried out. Belchatow clay (contained beidellite) slow down the crosslinking effect of the binder. The ratio of G"/G', modulus at low shear rates is less than 1, which indicates their liquid properties. Kaolin KOC (contained kaolinite) make grain aggregates with greater mechanical strength. The ratio of G''/G' modulus at low shear rates is greater than 1, which indicates a greater share of elastic properties of such binders.

To sum up, sealing binders based on kaolin KOC exhibit different viscoelastic properties than binders based on Belchatow clay. Their properties inhibits possibility of application. The same applies to the kind of cement.

Keywords: Clay-Cement Sealing Binder, Viscoelastic Properties, Flow Curve

25 - ABS 87

MODELING THE THERMAL AND ELECTRICAL CONDUCTIVITY RELATION OF SYNTHESIZED DIAMONDS WITHIN FRACTAL NATURE ANALYSIS

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Improvement of novel materials could be very good development base for enhancement of new technologies. One of the most promising material of modern science is undoubtedly synthesized diamond. Because of variety of modern applications, the research in this area is becoming intensive. Utilization of this material made great step forward in many areas, beside the most known jewelry, also in producing microcomponents, in medical-surgery, as well as in high professional industry. These and others specific application of polycrystal diamonds, require permanently research and improvement of their properties. Although, the first synthesized diamond was created half a century ago using high pressure - high temperature (HPHT) method, diamonds created by chemical vapor deposition (CVD) method were much more convenient for application in so many areas. By applying CVD method, microcrystalline diamond (MCD) with grain size approximately 100 nm were created. Due to some disadvantages of MCD films, like values of hardness and Young's modulus, new nanocrystalline (NCD) and ultra-nanocrystalline (UNCD) diamond materials were developed, with average grains size of 5-100 nm and 3-5 nm, respectively. The properties of polycrystalline diamonds can vary depending on the consolidation process like composition and pressure of applied gases, filament setup and reactor geometry. In that sense, changing the parameters of consolidation process, there is a possibility to change the microstructure of thin films and understanding its fundamentals. Also, fractal nature analysis could contribute to the revealing possibilities for improvement of polycrystalline diamond films. During carried out experiments, it was observed that there is the influence of grain size on thermal and electrical conductivity - when the thermal conductivity is increasing then electro conductivity is decreasing and opposite. Relation between the structures and final properties of synthetized diamonds can be achieved by explaining these phenomena based on fractal nature.

Keywords: Diamonds, Electrical Conductivity, Fractal Nature Analysis

26 - ABS 323

ELECTRIC-FIELD-INDUCED PHASE TRANSFORMATION IN FERROELECTRIC MATERIALS STUDIED BY TEMPERATURE-DEPENDENT NONLINEAR DIELECTRIC CHARACTERIZATION

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Relaxor ferroelectrics are characterized for a broadened and dispersive permittivity peak in their temperature-dependent dielectric spectra near the ferroelectric to paraelectric temperature.[1] Meanwhile, ordinary ferroelectrics exhibit a second-order phase transition that is characterized by a sharp peak in the dielectric permittivity at a frequency independent temperature.[2] However, this second-order phase transition could be induced by a bias electric field.[3] Moreover, ordinary ferroelectrics show a low-temperature dielectric relaxation with a broad, dispersive and temperature-dependent permittivity peak similar to relaxor ferroelectrics.[4] The study of this temperature- and frequency-dependent dielectric spectra has proven to be a helpful tool to study several physical phenomena of the ferroelectric systems such as structural phase transitions and boundaries, space-charge relaxations, point defects relaxations, and other dielectric relaxations. On the other hand, both types of ferroelectrics show high nonlinear dielectric responses with the amplitude of the applied electric field.[5] The nonlinear dielectric response understood as the variation of the dielectric coefficient with the amplitude of the applied electric field is enhanced near the dielectric anomalies regions.[6] Taking into account the existence of electric-field-induced phase transformations in the ferroelectric materials and the correlation between the nonlinear dielectric behavior and the microstructure of these materials[3] is expected that a bias-electric-field modify the nonlinear temperature-dependent dielectric response. The variation of the dielectric spectra due to the bias-electric-field allow gaining insights on the microstructural transformations. This work shows that the analysis of the nonlinear temperature-dependent dielectric spectra could be a helpful tool to study the electric-field-induced phase transformations in ferroelectric materials from the dielectric point of view.

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Keywords: Displacive & Relaxor Ferroelec, Nonlinear Dielectric Character, E-Field-Induced Phase Transf

27 - ABS 119

INFLUENCE OF POROSITY, PORE CHANNEL SIZE AND GEOMETRICAL SIZES OF BIOIMPLANTS ON THEIR PERMEABILITY

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Investigation of bone bioimplants architecture is essential for the understanding the ingrowth of newly forming bone into the implants, i.e. osteoconductive properties which are connected with the porosity. The native bone tissue may be described as a material with open, interconnected macropores (hundreds of microns) which provide the required space (permeability) for blood vessels, nerves, etc. Thus, it is necessary to create different bone implants, like calcium phosphate ceramics, hydrogels and composites, with the specific architecture of macropores that will facilitate high permeability and better osseointegration. In this work, we examined cellular architectures (Kelvin-type) and triply-periodic minimal surfaces (gyroid- and diamond-types) as models of porous bodies. Modelling the water and blood flow through the pore structure allowed us to estimate the permeability of various architectures by computer hydrodynamic calculations using Navies-Stokes equations. Modelling was carried out using SolidWorks 2013 software (Dassault Systèmes SolidWorks Corp.) with additional FlowSimulation module. Permeability of structures (k, darcy=d) was calculated according to Darcy's law: $Q=k*(P*A)/(\mu*h)$, Q – volume flow rate (m^3/s), P – pressure drop (Pa), A – cross-sectional area (m^2), μ – dynamic viscosity (Pa*s), h – height of cylinder (m). Total porosity was varied from 50 to 80%. Pore channels had two directions: (100) and (111) and size from 500 μm to 1,5 mm. Also, we varied the diameter and height of the cylinder models (suitable for small laboratory animals).

The models with the permeability about 1000 d that is similar to trabecular bone used for stereolithography 3D-printing of calcium phosphates bioceramics and calcium phosphate/hydrogel composites and further biomedical investigations.

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Keywords: Osteoconductivity, Permeability, Hydrodynamic Calculations

28 - ABS 795

SiC/NANO-DIAMOND CERAMIC COMPOSITES SINTERED BY SPS

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Ceramic materials with enhanced wear resistance are great interest for modern industry. Silicon carbide (SiC) can be ideal candidates for variety of applications, since it has superior properties in terms of wear, corrosion and oxidation resistance as well as excellent thermal shock and high temperature mechanical behavior. Thus considerable efforts are being made to improve more the wear and hardness behavior of the different applications made by SiC ceramics. Diamond reinforced SiC composite has a great attention due to their unique mechanical properties and it is potential usage for a various applications requiring high wear resistant. Based on the numerous literature, it is clearly indicate that interfaces in the diamond reinforced SiC ceramic composites play a special role for the mechanical properties of the composites, hence in this work I study the effect of nano-diamond incorporation on SiC ceramics with special attention to the interface phenomena between the SiC and the nano-diamond phases.

In this work, SiC based ceramics incorporated with nano-diamond in various amounts have been fabricated by novel spark plasma sintering (SPS) method. The different sintering temperature and phase composition are studied, where the nano-diamond powder is coated with and without silicon (Si). The microstructure, especially the interface between diamond and silicon carbide, are investigated by several methods. The chemical composition of the nano-diamond reinforced SiC composites are characterized by X-ray Photoelectron Spectroscopy (XPS). Distributions of residual surface stresses in diamond crystals were obtained by the analysis of Raman band shifts and splitting. The microstructure of the interface between the SiC and nano-diamond are studied by high resolution transmission microscopy (HRTEM) pay special attention to the studied the effect of the SPS process, as well.

Keywords: SiC, diamond

29 - ABS 774

HYDROTHERMALLY CRYSTALLIZED ZrO_2-MgO NANOPOWDERS. WAY OF PROCESSING AND PROPERTIES

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It is well recognized that some oxides form with zirconia solid solutions. It leads to the retention the tetragonal symmetry ZrO2 at low temperature. Such materials show interesting thermo-mechanical properties. In case of zirconia-magnesia system the staring powders were usually prepared by the high temperature treatment of the relative oxides mixture. This way of processing results in the coarse powders which have to be intensively ground. Quite different method was applied in the present study. It allowed us to receive the ZrO2-MgO solid solution powder of nanometric crystallite sizes. The starting aqueous solution of ZrOCl2+MgCl2 was introduced to the precipitating medium and the resulting co-precipitated gel was filtered and then subjected to the hydrothermal treatment for 4h at 240oC. Magnesium introduced into the system corresponded to 9 mole% of MgO in zirconia solid solution. Three different ways of the precipitating method were applied:
1. The starting ZrOCl2+MgCl2 solution was introduced to the vigorously mixed ammonia solution. The final pH was about 10 and the resulting gel was washed with distilled water.
2. (CH3)4NOH solution was the next precipitating agent. Also in this case the final pH was ~10 and washing with distilled water was also used.
3. Finally in the next method also aqueous NH3 solution was applied but the co-precipitated gel was washed with ammonia keeping pH of the filtrate at ~10 level.
Such materials were hydrothermally treated under the above shown conditions. Filtrates after the precipitation and hydrothermal treatment were analysed for Mg. The following numbers show how much Mg was removed from the system in relation to the starting magnesia introduced to the system: method 1 – 26.8% , method 2.-13.7% and method 3-1.6%. It indicates that the third technique gives the best results.
The materials prepared by the above described methods were subjected to the freeze drying and analysed by the X-ray diffraction. Tetragonal symmetry ZrO2-MgO solid solution was the majority phase of the nanometric crystallite sizes: Method 1 – 90.6% of tetragonal phase and 9.1nm crystallite sizes, method 2 – 72.1% of tetragonal phase and 8.1nm crystallite sizes and method 3- 88.5% of tetragonal phase and 9.6nm crystallite sizes. The powders were compacted and sintered. Density, phase composition and microstructure of the resulting materials will be shown.

The work was financially supported by the Polish National Science Centre under grant nr. 2017/25/B/ST8/02017

Keywords: magnesia stabilized zirconia,TZP,microstruture

30 - ABS 729

MECHANICAL PROPERTIES OF Cf/SiC COMPOSITE USING A COMBINED PROCESS OF CHEMICAL VAPOR INFILTRATION AND PRECURSOR INFILTRATION PYROLYSIS

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Cf/SiC composites were prepared via a process combining chemical vapor infiltration (CVI) and precursor infiltration pyrolysis (PIP), wherein silicon carbide matrices were infiltrated into 2.5D carbon preforms. The obtained composites exhibited porosities of 20 vol % and achieved strengths of 244 MPa in air at room temperature and 423 MPa at 1300°C under an Ar atmosphere. Carbon fiber pull-out was rarely observed in the fractured surfaces, although intermediate layers of pyrolytic carbon of 150 nm thickness were deposited between the fiber and matrix. Fatigue fracture was observed after 1380 cycles under 45 MPa stress at 1000°C. The fractured samples were analyzed by transmission electron microscopy to observe the distributed phases.

Keywords: CMC,chemical vapor infiltration,CFD

31 - ABS 802

NEW FUNCTIONAL PROPERTIES OF HIGH ENTROPY OXIDES

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Very recently, the configurational disorder has been used to create new oxide phases, extending the concept of high-entropy alloys (HEA) previously developed [1]. These new oxide phases were named “entropy stabilized oxides” or “high-entropy oxides” (HEOx) by analogy with the high entropy alloys. In a pioneering study that described the synthesis of these oxides, Rost et al. showed that heating an equimolar mixture of Mg, Co, Ni, Cu and Zn binary oxides at sufficiently high temperature followed by quenching, a single phase compound can form with the cations randomly distributed on one of the face centered cubic (FCC) sublattices of a rocksalt structure, the other one being occupied by oxygen. The HEA are a class of compounds thoroughly studied, revealing promising for a great variety of applications especially due to their exceptional mechanical properties, but also for magnetic electrical, chemical properties, hydrogen storage and other various applications. It is clear that unexpected new properties will be possibly discovered by exploring the HEOx and will lead to new applications. An interesting characteristic of HEO is the high Li-ion conductivity (10(meno3) S cm(meno1)), that is at the base of their storage capacity and cycling stability very appealing for the electrochemical field [2]

In this work we synthesized by conventional solid state (SS) synthesis at different temperatures the (Mg,Co,Ni,Cu,Zn)O oxide as well as its analogouses with four equimolar cations obtained by removing one of the cations. The same samples were also synthesized by Spark Plasma Sintering (SPS) and the same technique was also used for the sintering of the SS samples. The stability and existence of a single phase as a function of the sample stoichiometry were verified for both synthesis routes.

The samples were characterized by different experimental techniques. X-ray diffraction allowed to verify the formation of a single cubic rock-salt phase and the Rietveld structural refinement was used to determine the main structural parameters as well as the amount of eventual secondary phases. Spectroscopic techniques (Raman and EPR spectroscopy) were applied to determine the influence of the different cations on the octahedra vibrational properties, while EPR to verify the oxidation states of the transition metal cations. To explore possible new functional properties we determined the electrical conductivity, the magnetic behaviour and the thermoelectric properties of the samples.

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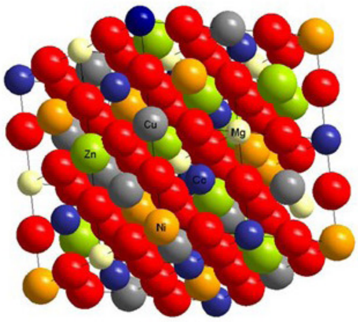
Keywords: High entropy oxides,Electric properties,Magnetic properties



Scheme of the Rocksalt structure of (Mg,Co,Ni,Cu,Zn)O HEO

32 - ABS 712

THE INFLUENCE OF SHELL MOULDS STRENGTHENED BY GLASS FIBRES AND METAL POWDERS IN THE TURBINE BLADES CASTING PROCESS

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The reduction of costs in the investment casting process involves the number reduction of low-quality components which are one of the basic problem of the foundry industry. Prevention of foundry defects is accomplished by optimizing the parameters of the metallurgical process and by optimizing the construction of shell moulds. Prevention of defects generated by causes dependent on the quality of the shell mould can be realized by refining the quality of technological and reinforcing materials for the mould construction and by optimizing the parameters of their manufacturing process.

Investment casting using multi-layered ceramic moulds allows manufacturing of geometrically complex components of the aircraft engine, such as turbine blades, vanes and casings. Operating under harsh condition that include high pressure and temperature above 1000C cause that the above mentioned elements are usually called critical components of the jet engines. In the investment casting process, the building of ceramic shells around the wax pattern is mainly time-consuming stage. The ceramic shell mould should be thick enough to withstand the thermal stresses generated during the pouring of the molten superalloy. Increasing the number of layers, on the one hand, ensure sufficient mechanical properties but also elongates the whole process including drying time and preheating of mould. The most of the moulds cracking occur at edges and sharp turnings, therefore the number of shells should be relatively low. Shell moulds for casting superalloy were strengthened by glass fibres included in the slurry and Ni-metal powder in the coverage. Castings were subjected to microstructural investigations in order to verify if the new design can be promising for manufacture of jet engine components.

Keywords: investment casting, ceramic shell, aviation

33 - ABS 701

OBTAINING OF THE COMPOSITE OF BETA-SIALON MATRIX VIA METAL-THERMAL AND NITROGEN PROCESSES IN THE B_4C-SiC-Al_2O_3-Si-Al-CARBON FIBER-GEOPOLYMER SYSTEM

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Obtaining of composite in the B N - Sic- beta S I A I O N-Al 203 system with the metal-thermal method in the nitrogen medium. In the present paper beta - S I A L O N-containing composite was obtained through alum-thermal process in the nitrogen medium on the base of Geo polymer (kaolin – Ukraine), B 4 C, Sic, Al 203, aluminum nano - powder and Si powder with small additives of per lit (A r a g a t z, Armenia) and carbon fiber by the reactive baking method. The advantage of this method is that compounds, which are newly formed thanks to interaction going on at thermal treatment: Si 3 N 4, Si, Al N are active, which contributes to beta - S I A L O N formation at relatively low temperature, at 1250-13500 C. It is evident that inculcation of AL N in crystal skeleton of beta -Si 3 N 4 is easier since at this temperature interval crystal skeleton of Si 3 N 4 is still in the process of formation. Beta S I A L O N was formed at 14500 C. Boron carbide was transformed into boron nit ride in nitrogen environment. Porosity of nit ride, oxide, carbide, beta -S I A L O N composite obtained by reactive s interring, according to water absorption, equals to 13-15%. The samples were fragmented in a jaw-crusher and were powdered in attrition mill till micro-powder dispersion was obtained. Then samples were hot-pressed at 18000 C under 30 MP a pressure. Hold-time at the final temperature was 8 min. Sample water absorption, according to porosity, was less than 0.3%. It should also be stated that strength and wear resistance of beta - S I A L O N s increase in their presence in silicium carbamlde containing composites. -he paper offers processes of formation of B N – S I c - beta - S I A L O N-Al 203 composites and their physical and technical properties. Phase composition of the composites was studied by X-ray diffraction method, while the structure was studied by the use of optic and electron microscope. Obtained materials are used in protecting jackets of thermos couples used for melted metal temperature measuring and for constructions used for placing objects in factory furnaces.

Keywords: nitrogen medium, alum-thermal process, composite

34 - ABS 667

RECYCLED SINTERED SODA-LIME GLASS AS SUBSTRATE FOR GRAPHENE

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Graphene has excellent mechanical strength, high electrical and thermal conductivity and optical transparency that serve as complementary components to those of glass. The combination of graphene and glass would offer electrical/thermal conductivity and surface hydrophobicity without sacrificing the transparency of conventional glass. The sodium inside the soda-lime glass creates high electron density in the graphene. Soda-lime glass thus offers a potential alternative to chemical doping, in which the electronic properties of graphene are optimized for use in devices. Soda-lime glass culets are sintered and their properties, in conjunction with graphene, are determined using FTIR, spectroscopy, DTA-TG and electrical conductivity. The results are promising for the use as substrate for graphene.

Keywords: soda-lime glass,graphene,sintering

35 - ABS 647

ELECTRICAL AND MECHANICAL PROPERTIES OF ALUMINA DOPED WITH TRANSITION METAL OXIDES SINTERED AT 1400°C

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Corundum (alpha-alumina) is one of the most exploited materials in ceramic industry due to its good physico-chemical properties, mechanical properties, and, importantly, due to its low cost. Advantageous properties, such as hardness, dielectric and thermal properties, and refractoriness, open the door to a wide range of applications of corundum. Porous alumina ceramics is often used for filters and as a catalytic substrate, whereas dense alumina ceramics is frequently used in automotive and aerospace industry. Hence, there is a great interest in exploring this type of ceramics. The aim of this work is to explain the influence of preparation parameters (mechanical activation, addition of transition metal oxides, and sintering conditions) on the final electrical and mechanical properties of alumina.

As a starting powder, a mix of a few alumina modifications (α-, κ-,γ - Al2O3) was used. It was doped with 1 wt % of Mn2O3, Cr2O3, and NiO, respectively. Three of the obtained mixtures were homogenized and three were ball milled for 60 min. Particle size analysis, SEM, and EDS were performed in order to demonstrate changes in the microstructure after milling. DTA/TG analyses were used to determine all characteristic temperatures. After sintering at 1400 oC in an air atmosphere, mechanical, electrical, and physico-chemical properties of the obtained ceramics were determined.

Results showed that the mechanical treatment lead to a decrease in temperatures of phase transitions and sintering for approximately 100 oC. Incorporation of cations of transition metals into the crystal lattice of alumina was noticed. Activated and sintered samples showed a higher tensile strength and higher relative dielectric permittivity then the sample doped with Cr2O3.

The main conclusion of this investigation is that the mechanical activation has the dominant influence on lowering the characteristic temperatures of all detected phase transitions and sintering processes. Using a mixture of several crystalline phases of alumina as a starting powder alleviates the incorporation of transition-metal cations into the alumina crystal lattice, leading to changes in microstructures of the prepared ceramics. Finally, changes in the microstructure and lattice disordering have the dominant influence on the final mechanical properties.

Keywords: alumina, sintering, dopants

36 - ABS 592

STRUCTURE AND CONDUCTIVITY OF 9CaO-91ZrO$_2$ CERAMICS, OBTAINED FROM FREEZE-DRIED POWDER WITH CRYOPROTECTANT ADDITION

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The elimination of the agglomeration degree in the zirconia based precursors during its synthesis and processing is critical for further advanced ceramics manufacturing. So far, to ensure the aggregative stability of nanosystems, the stabilizers, i.e. surfactants are mostly used. However, their removal is complicated and it often leads to drastically conductivity decrease of the final ceramic solid electrolyte. Acetone can play the role of a surfactant, which is easily removed from the system during the dehydration. In case freeze-drying is used for dehydration, it also turns to be a cryoprotectant, diminishing the size of water crystals and preventing the possible change of precursors microstructure. Thus, the aim of this work was to study the effect of the synthesis medium on the phase formation and agglomeration in 9CaO-91ZrO2 (mol.%) precursors during their thermal evolution as well as structure and conductivity of the ceramics.

Precursor was prepared by sol-gel synthesis in a way of the reverse co-precipitation. Decimolar solution was prepared using the starting salts ZrO(NO3)2·5.5H2O, Ca(NO3)2·2H2O. Precipitation of amorphous hydroxides was carried out from water-acetone solution with various acetone content (1M aqueous ammonia was used as a precipitate, T = 1-2°C, pH = 9-10). The precipitate of hydroxides was dehydrated by freeze drying. The obtained amorphous samples were calcined at different temperatures (200-1100°C) for 2 hours to subsequently track the thermal evolution of the system. Based on the data obtained solution containing 7 vol.% acetone was chosen for further ceramics fabrication. Precursor was compacted into the pellets with a diameter of 10.5 and ~4 mm thickness at P ~3.5 kg/cm^2 and annealed at 1550°C for 3 hours in air. The samples obtained were comprehensively studied by STA, BET adsorption-desorption isotherms, XRD, SEM and Impedance spectroscopy.

Via SEM and adsorption-desorption it was found that precipitation from a solution containing 7 vol.% of acetone results in flake-like powder having microporous structure and a relatively low specific area of 110.2 m^2/g. It was proved that the extended area of a cubic zirconia based solid solution existence, namely 600-1100 °C, is due to high dispersity of the precursor and nanosized crystallites in the entire studied temperature range. It was shown that crystallinity degree of solid solution increases with the increase of temperature. Temperature dependence of the integral conductivity was obtained. Grain and grain boundaries impacts to the internal conductivities, as well as activation energy were established.

Keywords: Agglomeration, Cryoprotectant, Precursor

37 - ABS 574

TOUGHNESS AND DIELECTRIC BEHAVIOR OF POLYCRISTALLINE ALUMINA

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Different alumina materials were elaborated in order to vary micro structural parameters (grains size, densification, porosity, intergranular phase). These ceramic materials were then characterized from the mechanical point of view (hardness, toughness, friction and wear) and dielectric breakdown. The comparison of these various results shows that for all these properties, the grain size and, thus also, nature of the secondary phases are the most discriminating microstructural parameters.

Moreover from the tribological point of view, the dielectric characteristic of materials (breakdown strength) has a fundamental role on the creation of the third body and the properties of this last: a finely agglomerated third body will be obtained for high breakdown strength. Such third will be able to protect the substrate and thus to reduce later wear. In same logic a correspondence between breakdown strength and toughness was established, thus confirming the mechanics-electric correlation existing for the non-conductive materials.

Keywords: Breakdown, Toughness, Wear resistance

38 - ABS 545

PREPARATION OF TRANSLUCENT ALUMINA CERAMICS THROUGH SLIP CASTING AND VACUUM SINTERING

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This study is to prepare translucent alumina ceramics through slip casting and vacuum sintering.
Alumina green bodies doped with 0–2000 ppm Mg2+ were prepared by slip casting. A dispersant, PAA-NH4, was added in order to lower slip viscosity. Pre-heating at 800°C/12 h eliminated fine particles, decomposed magnesium nitrate and the dispersant, and reached 66% green density. Sintering was done in vacuum at various temperatures, holding times, and heating rates in furnaces A and B.
The results show that the bodies with 1000 ppm Mg2+ has high transmittance after sintering at 1700°C/1 h in furnace A. The sintered density reached 99.4% and the real-in-line transmission was 6.93%. The hardness and fracture toughness were 16.26 GPa and 3.25 MPa.m1/2, respectively. Sintering in vacuum at 1700°C/1 h was also done in furnace B, and 98.8% density was obtained. The real-in-line transmission was 2% due to numerous micro-pores. The hardness and fracture toughness were 17–18 GPa and 3.25 MPa. m1/2, respectively.
Translucent alumina ceramics were successfully prepared through slip casting and vacuum sintering.

Keywords: slip casting, vacuum sintering, translucent

39 - ABS 537

SYNTHESIS OF Ti-, Zr- AND Hf-CONTAINING MAX CARBIDE PHASES BY ELECTRIC ARC FURNACE AND BY SPS

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MXene phases are bi-dimensional carbide or nitride phases with original properties that have generated interest in domains such as energy storage [1,2], electronics [3,4] or even catalysis [5]. These phases are synthesized by ablation of MAX phases whose composition flexibility leads to the optimization of their properties and those of the associated MXene phases.

In this study, synthesis of the M2AlC MAX phase by arc discharge and Spark Plasma Sintering (SPS) from M (transition metal: Ti, Zr or Hf), Al and MC powders have been carried out. To increase the proportion of the target-phase in the samples and limit the proportion of secondary phases, the synthesis parameters have been optimized.

The optimization of the intensity of the arc and duration of the heating in the electric arc furnace were carried out to obtain the desired composition, i.e. to limit the proportion of secondary intermetallic and carbide phases.

By using SPS, the sintering cycle was imagined in two parts: a first hold, at a relatively low temperature to limit the aluminum vaporization, to allow for the formation of intermetallic phases from the elemental M and Al powders, which can then react during the second hold at higher temperatures with the MC powder to form the carbide MAX phase. The temperature, holding time and load applied were optimized to limit the formation of unwanted phases. Pressure-less cycles, where no load was applied to the sample during the sintering, were also studied.

In the Ti-Al-C system, the samples synthesized by arc discharge contained up to 60 wt.% of the 211 phase . Nevertheless, the 312 phase was always present as a secondary phase, alongside TiC.

By using SPS, a sample containing only the 211 phase was obtained through the pressure-less cycle. It was composed of a first hold at 600 °C for 15 min and a second one at 1200°C for 10 min. In the case of load application (75 MPa), the best sample contained around 87 % of the Ti2AlC phase and was fabricated with the same temperature cycle as above.

Experiments regarding the synthesis of the Zr- and Hf- containing MAX phases are still on-going.

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Keywords: MAX phases,Electric Arc Furnace,Spark Plasma Sintering

41 - ABS 503

THERMAL CYCLING BEHAVIOUR OF ALUMINA-SPINEL CASTABLES

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Introduction Alumina-spinel castables are being increasingly used is steel-making applications like steel ladles. Although, these materials have been the focus of research since the late 1980s, the thermo-mechanical degradation phenomena under continuous thermal cycling conditions have not yet been thorough investigated. The objective of this proposed work is to assess the thermal stability and cyclic fatigue resistance of alumina-spinel castables with varying microstructure and varying spinel contents.The study of gradual fatigue of alumina-spinel castables due to thermal cycling forms a vital part the EU MSCA ITN ATHOR (Advanced THermomechanical multiscale mOdellingof Refractory linings) project.

Materials and Methods Various model castable formulations were designed in order to investigate the influence of spinel content, binder type: standard calcium aluminate cement vs. novel calcium magnesium aluminate binder and the nature of the aggregates: tabular alumina vs. white fused alumina. The microstructure of samples before and after thermal cycling were investigated by scanning electron microscopy associated with energy dispersive X-ray spectroscopy (SEM-EDS) analyses. Samples were thermally loaded with the use of High Temperature Thermal Shock Furnace by slight high temperature thermal cycling between two high temperature limits. Material behavior under thermal cycling conditions was then evaluated by means of Young's modulus, mechanical damping and Acoustic Emission measurements.

Results and conclusion Continuous monitoring of Young's modulus value and damping behavior versus temperature provides substantial information about the microstructural alterations taking place in the material exposed to thermal cycling conditions. Acoustic Emission activity variations is be correlated with changes in Young's modulus value in order to characterize the fracture process and investigate its influence on material behavior at intermediate temperatures. It will be demonstrated that all three techniques should be seen as a set of complementary methods providing undetectable by other techniques information about material behavior under thermal cycling conditions.

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Keywords: Thermal cycling, Alumina-spinel castable

42 - ABS 482

DEVELOPMENT OF CERAMIC BASED STATIONARY PHASES FOR CHROMATOGRAPHY

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Preparative chromatography is still manly performed with silica-based retention phases. The low mechanical and chemical stability range of silica limits the possible parameter space of chromatographic protocols. In order to fully protonate or deprotonate common product types or to routinely clean and reuse the columns at high pH, stationary phases with stability ranges outside pH 2–10, monomodal size distribution, controlled porosity and pore size, and higher mechanical strength would be desired. Current work shows promising results with ceramic oxide materials, such as alumina (Al_2O_3), titania (TiO_2), or zirconia (ZrO_2).

Porous spheres of zirconia, alumina and titania were produced either by a precursor route or by controlled agglomeration of nanoparticle dispersions. In the former approach, ceramic precursor solutions were either dispersed by agitation or dispensed dropwise into a curing bath. After calcination, particle sizes and pore sizes of the formed porous particles were compared in the prepared state and after surface modification with different polymers. The stability against dissolution of various materials was tested in buffer solutions at pH 1 and pH 12.

Dispensing methods have the advantage of easier control over the particle size in comparison to droplet formation by dispersion of the precursor solution. In both cases, the targeted particle size of 10-30 µm could be reached. While particles formed by aggregation show enhanced surface area, their particle size is smaller than desired (1-10 µm), leading to increased back pressure in the column. Additionally, a simple process was developed to modify the particles surfaces with different acrylic polymers for derivatization.

Non-silica-based inorganic porous spheres were synthesized and used for chromatographic tests. Promising results show the potential of such materials, but further refinement of process conditions is required to improve control over important parameters such as particle size and pore size.

Keywords: porous particles, non-silica stationary phase, chromatoraphy

43 - ABS 464

EXAMINATION OF MULLITE CERAMIC SPECIMENS MADE BY CONVENTIONAL CASTING METHOD FROM KAOLIN AND SAWDUST

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By using relatively low-cost materials (conventional kaolin and sawdust powders) and technology the authors have developed new ceramic composite materials which can meet successfully different industrial requirements. Casting masses were made by milling different compositions of the powders and by adding distilled water. The test specimens were made by conventional gravitation casting method and after the drying process the specimens were sintered in an electric kiln under oxidation and oxygen-free atmosphere at 1250°C max sintering temperature. The prepared and sintered specimens were tested on geometrical sizes, microstructures and morphologies by scanning electron microscopy. In this work the authors present some parts of the results of their research and investigation.

Keywords: ceramic, mullite, sintering

44 - ABS 364

HYDROTHERMAL DEGRADATION IN ZIRCONIA COMPOSITES WITH DIFFERENT BIDIMENSIONAL GRAPHENE-BASED NANOSTRUCTURES

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This work is devoted to assess the influence of the incorporation of different amounts of two-dimensional graphene-based nanomaterials (GBN) on the hydrothermal degradation resistance of zirconia (3YTZP). Different powder processing routines and spark plasma sintering have been used to obtain dense and submicrometric tetragonal zirconia composites with 1, 2.5 and 5 vol% of two different GBN, respectively: few layer graphene (FLG, less than 3 graphene layers) and graphene nanoplatelets (GNP, 10–20 nm thickness). The microstructure of the sintered composites has been characterized to evaluate the preservation of the graphene-based nanostructures, their degree of dispersion in the ceramic matrix and the ceramic grain size distribution. The intrinsic effect of the different GBN addition (type and amount) on the spontaneous transformation of the zirconia tetragonal phase to monoclinic phase has been explored by conducting accelerated hydrothermal degradation experiments in autoclave. X-Ray diffraction has been performed on the composites as well as on the monolithic 3YTZP to quantify the monoclinic phase content before and after the aging experiments in order to establish the hydrothermal degradation kinetic curves of these materials.

Keywords: zirconia, graphene based nanostructures, hydrothermal degradation

45 - ABS 298

CLAY CATALYTIC ACTIVITY Na35 BENTONITE IN BIODIESEL PRODUCTION

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Natural clays are known to present a low catalytic potential in organic reactions and low adsorption capacity. This work aims at obtaining modified clay natural sodium bentonite Na35 using the pillarization with zinc acetate and tin chloride was carried out in order to be used in the biodiesel production process. When pilarizated, the octahedral face is modified resulting in change in the structure, chemical composition and in the clay physical properties. The adsorption/ desorption N2 isotherms of the BET model, X-ray diffraction (XRD), scanning electron microscopy (SEM) and 27Al nuclear magnetic resonance (27Al NMR) were characterized. Subsequently, these catalysts were used to obtain biodiesel by heterogeneous catalysis. The obtained biodiesel, characterized by 1H NMR, showed a conversion rate in methyl esters of fatty acids of 96.5%. Thus, showing the efficiency of Na35 bentonite catalysts pillarized in the production of biodiesel.

Acknowledgments
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Keywords: heterogeneous catalyst, pilarization, modified clay

46 - ABS 296

ULTRAFINE FIBROUS CERAMICS WITH IMPROVED MECHANICAL PROPERTIES GROWN BY THE LASER-HEATED FLOATING ZONE TECHNIQUE

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This research work is a pioneering contribution on the fabrication of ultra-fine fibrous microstructure MgAl2O4-MgO eutectic ceramics by the laser-heated floating zone (LFZ) method. MgAl2O4-MgO eutectic ceramics can be optimally grown at 750 mm/h, resulting in ultra-fine fibrous eutectic ceramics free from transverse cracks. Lower growth rate below 750 mm/h causes coarsening the fibre interspacing which is detrimental for the mechanical properties and catastrophic decrement happens for 50 mm/h growth rate with the presence of transverse cracks. In terms of mechanical properties enhancement, MgAl2O4-MgO eutectic ceramics fabricated at 750 mm/h growth rate favourably showed elevated hardness (15.5 GPa from Vickers indentation and 22 GPa from nanoindentation), fracture toughness (2.7 MPam½) and strength (260 MPa) compared with spinel matrix.

Keywords: MgAl2O4-MgO eutectic, laser floating zone, mechanical properties

47 - ABS 256

INVESTIGATION OF SINTERING PARAMETERS FOR CONSOLIDATING ALUMINUM NITRIDE CERAMICS

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Aluminum nitride is a promising material for applications that require electrically insulating substrates with high thermal conductivity. However, the material has to be dense and of high purity. Porosity as well as impurities, e.g. oxygen substituting nitrogen in the lattice, or an oxide layer covering the grains, strongly limit the thermal conductivity. Sintering additives like yttrium oxide or calcium oxide can be used to aid in the densification of the material, thus increasing its thermal conductivity.

The objective of this work is the evaluation of a variety of aluminum nitride powders and powder mixtures with sintering additives consolidated by sintering at ambient pressure or by hot-pressing, with the goal of correlating processing parameters with physical properties of the obtained ceramics, including density, hardness, and bending strength.

Two aluminum nitride powders with different grain sizes and purities were used in combination with yttrium oxide and calcium carbonate as sintering aids. The powder mixtures were prepared by mixing in isopropanol using a planetary rotary mill followed by dry mixing using a shaker mixer.
Prior to sintering at ambient pressure, the powders were compacted by cold isostatic pressing before being fired at 1700 °C for 2 h in nitrogen atmosphere.
In contrast, hot-pressing was conducted at 1800 °C and 35 MPa for 2 h in nitrogen atmosphere, using powders without prior compaction.
Subsequently, structural, thermal, and mechanical properties were determined for the consolidated samples.

The experiments confirm that sintering additives are critical for the densification of aluminum nitride at ambient pressure, whereas hot-pressing leads to dense ceramics even without sintering additives. It was shown that other properties are dependent on the addition of sintering additives as well, including hardness, bending strength as well as thermal conductivity. In case of mixtures containing sintering additives, SEM imaging confirms an even distribution of the sintering aids within the mixtures, with secondary phase present in triple grain junctions.

While hot-pressing was shown to yield ceramics with high density values even without the addition of sintering aids, processing parameters such as type and quantity of sintering additives, temperatures and holding times have to be fine-tuned in order to consolidate aluminum nitride at ambient pressure and, consequently, to obtain desirable mechanical and thermal properties of the resulting materials.

Keywords: Aluminum nitride, Hot-pressing, Thermal conductivity

48 - ABS 931

DENSE ALUMINA MULLITE COMPOSITE CERAMICS FROM ALUMINA AND A SPODUMENE-ALBITE FELDSPAR BINARY MIXTURES. PROCESSING AND PROPERTIES

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Alumina materials are a family of ceramic materials whose main component is aluminum oxide (Al2O3). These are frequently used in the production of structural ceramics due to their high availability, low cost and mechanical properties; they are also widely used in various industrial applications. Spodumene (LiAl (SiO3)2) is a natural silico-aluminate, it is generally used for the manufacture of ceramic enamels and as a source of lithium salts (carbonates and hydroxides) through hydrometallurgical routes. In natural ores the spodumene is usually accompanied by quartz, and soda feldspars.

In the present work dense structural ceramics are presented based on materials elaborated from calcined alumina and an industrial spodumene. The employed spodumene was characterized; both chemical and mineralogical compositions were evaluated. The proportion of the sintering additive in the range 15 – 45 % w/w at 1400 ° C has been explored (AS15-45). The developed crystalline phases identified by X-ray diffraction and quantified using the Rietveld method. Also, the microstructures developed by scanning electron microscopy (SEM), the textural properties (density and porosity) and the mechanical properties were studied: bending at 3 points (σf) and dynamic elasticity module (E). The coefficient of thermal expansion (α) of the materials obtained was also evaluated. Finally, the processing variables were correlated with the technological properties. Materials were obtained containing as main phases alumina (Al2O3), mullite (3Al2O3.2SiO2) and glassy phase.

The proposed route permitted to process dense ceramic materials with fine microstructure. The sintering mechanism observed implied the thermal transformations of the spodumene and albite with the corresponding mullite formation. The results obtained encourage the application of the chosen strategy. Porosity materials of less than 2% were obtained with adequate technological properties (σf, E). It should be noted that the value of the coefficient of expansion was reduced by the addition of the spodumene.

Evidently the materials correspond to alumina materials. The AS15 corresponds to an alumina sample with small amount of mullite phase and glass as sintering aid. On the other side the AS45 corresponds to a composite with alumina and mullite as principal phases. AS30 is an intermediate proportion and presents the better properties. 181 MPa flexural strength and 5.7 x 10-6 °C-1 thermal expansion coefficient were achieved.

Keywords: composite ceramics, spodumene, processing and properties

49 - ABS 151

STUDY ON THE TRANSFORMATION PROCESS FROM METALLIC POLYMER PRECURSOR TO SOLID SOLUTION $HfTaC_2$

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Synthesis of polymer precursor HfTaC2 (HTC) was accomplished via coordination reaction of metal alkoxides with acetylacetone and hydrolysis, organic polymer novolac resin was introduced as carbon source subsequently. Particular emphasis was given on polymer-to ceramic mechanism. Analysis of transformation process was performed on in-situ XRD and synchrotron radiation wide angle X-ray scattering (WAXS). Data collected illustrated that intermediate phase Hf6Ta2O17 was detected to appear firstly at ~950 °C, followed by TaO, TaC, HfC and HfxTayCz solid solutions. Phase composition at increased temperatures revealed that: carbides were generated via carbothermal reduction reaction from oxides warehouse, including Hf6Ta2O17, HfO2, Ta2O5 and TaO; solid solution reaction of HfxTayCz continued simultaneously. Transition from metastable state (TaO) to steady state (Ta2O5), were also traced in-situ, furtherly expounded the complexed mechanism. Ceramic crystals of diverse sintering time were discussed by XRD, SEM, EDS, and laser particle size analyzer. HfTaC2 ceramic powder could be achieved at 1450 °C after sintered for 90min in vacuum with size distribution was around Dv (90)~200nm and well distributed elements.

Keywords: ultra high temperature ceramic, reaction mechanism, high temperature in-situ XRD

50 - ABS 130

CERAMIC COMPOSITE FOR MANUFACTURING OF ARMORED ELEMENTS

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Obtaining of ceramic composites with high hardness, high impact strength and low density for application in armored elements.
The novelty is a composition of the composite on the basis of B4C-SiC-BN-Al2O3, in which the best properties of the components are manifested synergistically.

The composites are obtained by the method of hot pressing at the conditions of temperature 1600-1800 oC and pressure 30 MPa.
new ceramic composites of several compositions are obtained by a new pressing method; they have high hardness (20-35 GPa), sufficiently high bending strength for this group of materials (300-395 Mpa) and high impact strength (15-24 kJ/m2).

The obtained materials by their physical and mechanical properties meet the criteria for materials used in armor, as compared with armor steel the parameter is 2-7 times higher, and compared with aluminum oxide – in 1.3 - 2.3 times higher.
As to armor material of boron carbide, by this criterium the researched composites are left behind in 1.5 - 2.6 times. On the other hand, boron ceramic is sintered at the temperature 2100- 2200 oC, and the composite, chosen by us, - at 1750 - 1800 oC.
The obtained result has been determined by selection of a composition, by dispersion of aluminum oxide and boron carbide (D50-500 nm); correct management of the process of sintering by hot pressin

Keywords: armor, boron carbide, hardness

51 - ABS 954

SINTERING PROCESSES AND PHASE FORMATION STUDY OF $MoSi_2$-$NbSi_2$ CERAMIC

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The creation of a modern composite material with electrical conductivity, high strength, viscosity, oxidation resistance and capable of withstanding multiple thermal cycling, requires thorough fundamental research. Recently studies of composites based on niobium are on the forefront. Even the introduction of 1 at.% Nb into molybdenum disilicide (MoSi2) lowers the transition of the material from brittle to ductile to room temperature [1]. In addition, the alloys of Nb with MoSi2 show a significant increase in the value of the flexural strength at 1600°C. Thus, the fundamental task of this paper is to thoroughly study the sintering processes and phase formation in the system (Mo1-xNbx)Si2 obtained by the SHS method [2]. The work will include the study of synthesis processes and the search for new ways of obtaining composites of a given composition (Mo1-xNbx)Si2 in steps of 10 wt.% NbSi2, the dilatometric study of sintering processes and the establishment of patterns of composition effects on the change in the shrinkage temperature. Based on the dilatometry, the optimum sintering conditions for each particular ceramic composite will be selected by hot pressing. The obtained samples will be comprehensively studied by modern methods including X-ray, SEM, strength, Coefficients of Linear Thermal Expansion (CLTE) for each composition are obtained [3]. These data will be compared with the shrinkage curves and conclusions are drawn about the effect of the phase composition on the sintering process of a ceramic composite of a given composition. The pure MoSi2, NbSi2 and (Mo1-x,Nbx)Si2 solid solution, obtained by SHS method and solid-phase mixing, were studied up to 1900°C in Argon atmosphere by dilatometric analysis. It is shown that the continuous shrinkage curve of molybdenum disilicide and niobium has a similar relief. The two disilicides mixture shrinkage curve shifted Tonset to a higher temperature region. The (Mo1-x,Nbx)Si2 solid solution had a completely different shrinkage curve, it was characterized by a pick at 305°C and a double kink in the sintering process corresponded to the passage of two successive sintering processes. The x-ray analysis confirmed the change in lattice parameters in the temperature range from 280° to 320°C.

Keywords: dilatometry, disilicide, self-propagating high-temperat

52 - ABS 86

MONITORING OF REFRACTORY CASTABLES DRYING

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In recent decades, there has been an increasing use of hydraulic setting refractory castables. By comparison to refractory bricks, these materials often enable significant saves in time and money with same or higher performances. However the use of refractory castables is subjected to major risks of cracking or even explosion during the first heating of the plant. Indeed, the rise in temperature causes an increase of the steam pressure inside the material function of the evaporation and diffusion rates of the water contained in the castable (free and chemically bonded). Therefore, the dryout schedule has to be carried out with caution to keep this pressure lower than the mechanical resistance value of the material to avoid lining damages. Currently, refractory castables drying is performed following empirical dryout schedules. No heating protocol based on scientific arguments and no suitable monitoring tools for the drying have been proposed. Therefore, this study aims to better understand the drying behaviour of hydraulic setting refractory castables by using suitable in-situ monitoring tools (acoustic emission sensors, pressure sensors, stress and humidity sensors). A better understanding of the drying behaviour of these materials during the first heating would be helpful to define an optimal dryout schedule and then improve the material lining performance in service and their sustainability while reducing the energy consumption and also raw materials.

Keywords: Refractory castables, drying, monitoring tools

53 - ABS 202

DIRECTIONAL PROPERTY CHARACTERIZATION OF HOT PRESSED B_4C-TiB_2 COMPOSITES DOPED WITH WC

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Boron carbide (B4C) is one of the important non-oxide ceramic material due to its superior physical and chemical properties such as extreme hardness and low thermal conductivity. In order to improve the sinterability of B4C, sintering additives such as carbon, aluminum, silicon carbide, titanium diboride (TiB2) phases are added as sintering aid and these additives also improves the mechanical properties.

Aim of this study is the microstructural characterization of the hot pressed B4C-TiB2 composites as well as effects of uniaxial pressure during sintering over microstructure and mechanical properties. In this study, three different B4C-TiB2 (50:50 vol%) composite mixtures were used; (i) ball milled and (ii) high energy milled and (iii) ball milled B4C-TiB2 doped with 5 volume % of tungsten carbide (WC). All powder mixtures were sintered with hot pressing (HP) method and characterized by conventional SEM, TEM and STEM imaging methods. SEM analyses revealed the differences in microstructures as well as present phases between samples due to different processing conditions. Effect of milling method is significant in the particle size of the composites that is, high energy milling resulted with smaller particles. All samples mainly consist of TiB2 and B4C phases however, depending on milling conditions and WC addition, new Ti-W-B containing phases with different amounts of W were observed around TiB2 particles as core-rim structure. Core-rim structures around TiB2 particles were characterized in detail with STEM-EDX analyses.
Furthermore, production methods that include uniaxial pressing may end up with anisotropic properties of the produced materials, therefore microstructure and mechanical properties depending on the sample orientation relative to the pressing direction were investigated. According to the SEM images it was found that morphology and microstructure varies depending on the pressing direction and this difference also present in XRD analyses. Effects of texture on the mechanical properties were measured by hardness and indentation toughness depending on pressing direction and will be presented.

The authors would like to acknowledge the financial support from the Scientific Research Project Commission of Anadolu University (grant no:1504F168) and The Scientific and Technological Research Council of Turkey (TUBITAK) 2211 scholarship programme.

Keywords: Hot Pressing,TiB2-B4C composite, Microstructure

54 - ABS 313

ANISOTROPIC PROPERTIES OF SPARK PLASMA SINTERED IN-SITU W_2B_5-B_4C COMPOSITES

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In order to shield both gamma and neutron radiation without the need of two separate materials, W2B5-B4C composites were produced for gamma and neutron radiation attenuation applications. In this study, anisotropic effects due to the mechanical pressure during sintering on the mechanical and microstructural properties were investigated. After the preparation of various amounts of metallic tungsten containing B4C powders, composites were sintered by spark plasma sintering (SPS) technique. The sintering was carried out at temperatures of 1550, 1575 and 1600°C, 4 minutes soaking time under vacuum by applying 40 MPa uniaxial pressure. The hardness and fracture toughness of the samples were evaluated by the Vickers indentation technique and Palmqvist Method. Microstructures of the samples were investigated by using in-lens mode of scanning electron microscopy because of the ability to show fine graphite in B4C matrix. The phase investigation of spark plasma sintered samples was obtained by using x-ray diffraction. After SPS, W2B5-B4C composites were produced but the composites contained graphite as a result of the reaction between W and B4C. All characterization methods were applied both in and through pressing direction in order to analyze the effect of anisotropy. In this work, mechanical properties and microstructures of the composites will be discussed.

Keywords: Boron carbide, Spark plasma sintering, Anisotropy

55 - ABS 30

IN SITU SYNTHESIS AND CHARACTERIZATION OF B_4C-TiB_2 FIBERS COMPOSITES

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In this study, B4C/TiB2 fibers composites were fabricated using field assisted sintering technique. The boron carbide matrix composites containing 10-30 vol% TiB2 fibers were prepared by in situ reaction of B4C, TiO2 fibers and carbon black. The TiO2 fibers used in the study were prepared using needle-less electrospinning technique, followed by the heat treatment. The effect of TiO2 fibers additions on the sintering behaviour of B4C was studied in the temperature range of 1700 °C to 2100 °C and the pressure of 50-70 MPa.

The materials were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Raman spectroscopy. Results showed that TiB2 fiber is distributed uniformly in the B4C matrix. Only B4C and TiB2 phases were identified, although the presence of a small amount of oxygen or carbon could not be ruled out. This confirmed that the reaction between TiO2 and B4C was completed and no residual TiO2 was found in the materials. The full densification was achieved when applying an optimized loading cycle, in which the maximum load was applied after the completion of the B4C-TiB2 powder synthesis, allowing degassing of volatile species. The effect of the various TiB2 addition on the mechanical properties of B4C, such as hardness, fracture toughness, elastic modulus, strength and wear resistance, were investigated.

Keywords: B4C / TiB2 composites, In-situ reaction, Reactive sintering

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56 - ABS 67

THE INFLUENCE OF GRAIN SIZE ON THE DENSIFICATION AND MICROSTRUCTURAL EVOLUTION OF BORON CARBIDE CERAMICS DURING PRESSURELESS SINTERING

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Boron carbide as high-performance ceramics has distinguished and excellent physicochemical properties such as hardness, wear resistance, low density, etc. However, the preparation of well-formed boron carbide bodies approaching the material theoretical density remains challenging. In this study four different boron carbide powders with particle size ranging from ~ 0.5 μm to ~ 42 μm were used to investigate the effect of particle size, applied pressure during cold pressing and oxygen impurity content on the pressureless sintering behaviour at the temperature of 2200 °C in vacuum. It was found that B4C powder (powder “B”) with the average particle size of 1.5 μm shows the highest relative density (up to 93%). despite of bigger particle size in comparison to finer powder (powder “A” – D50 ~ 0.5 μm). The use of very fine powders leads to microstructural coarsening and pores evolution due to the presence of a greater amount of oxygen impurity. B4C samples sintered from powder „A“ and coarser powder „C“ (D50 ~7 μm) achieved comparable relative density. On the other hand the delamination connected with the low density was observed in samples prepared from powder (powder „D“) with average particle size about 44 μm.

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Keywords: Boron carbide, Grain size, Pressureless sintering

57 - ABS 65

COMPARISON OF CONVENTIONAL AND UNCONVENTIONAL SINTERING OF ALUMINA CERAMICS CONTAINING WASTE ALUMINA POWDER OBTAINED BY SLIP CASTING

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This paper reports the results of studying the alumina ceramics which contain a considerate amount of waste alumina powder. The study focused on the investigation of the conventional sintering and hybrid microwave sintering of alumina green bodies in which the grain growth and densification were characterized after sintering. Waste alumina powder was obtained by green machining. Alumina green bodies were obtained by the slip casting process. Stable concentrated aqueous alumina suspensions were prepared with the addition of 0.05 wt. % Tiron, 0.1wt. % PVA – poly (vinyl alcohol), 0.2 wt. % magnesium spinel and 20 wt. % of waste alumina powder (expressed on dry weight basis of alumina powders). The used hybrid sintering atmospheric furnace consists of a 2.45 GHz microwave generator with a continuously adjustable power output from 0 to 3 kW and external heating elements. The sintering time for microwave hybrid sintering was significantly shorter than for conventional sintering. After sintering, density, grain size, hardness, fracture toughness and microstructure of the samples were examined, and comparisons were made for the conventional sintering and hybrid microwave sintering methods.

Keywords: waste alumina, conventional sintering, hybrid microwave sintering

58 - ABS 51

SPS SINTERING OF ZIRCONIA TOUGHENED ALUMINA COMPOSITES WITH TITANIA ADDITION AND ITS EFFECT ON MICROSTRUCTURE

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The improved relative density and enhanced mechanical properties of nanostructures makes them attractive for technical research and application. The ideal sintering conditions for nano-composite ceramics is low temperature with minimum dwell time and rapid heating and cooling rate to inhibit grain growth. One of the recent processes used to successfully produce nanostructures is Current Activated Pressure Assisted Densification (CAPAD) also called Spark Plasma Sintering (SPS). In addition, titanium oxide is one of the additives which has been widely used in ceramics mainly as a sintering aid and is found to improve the fracture toughness and wear resistance of alumina ceramics, as well as enhance the density and augment tetragonal phase stability of zirconia ceramics. Although the effect of titania on structure and mechanical properties of alumina has been widely studied, there is not much research on its effect on zirconia toughened alumina (ZTA) composites, particularly in nano-sized ceramics. Thus, the current study examined the effect of titania addition on the microstructure of ZTA composites produced by SPS. The volume percent of Y-TZP used in this study was 15 vol.%, below the percolation limit of 16 vol.%. Composites containing no titania (pure ZTA), 0.1 mol%, 0.5 mol%, 2 mol% and 5 mol% of TiO2 were produced. All the samples were reasonably dense, with greater density at higher sintering temperature. No tangible effects of the dwell time on the relative density was observed. Small amounts of 0.1 and 0.5 mol% titania addition improved sinterability and densification of the samples; however, the relative density decreased for all sintering temperatures and times for higher content of titania to 2 and 5 mol%. Similarly, the titania addition increased grain growth with the increase greater for alumina than zirconia. XRD and SEM studies showed that titania first dissolved in zirconia to form a tetragonal zirconia solid solution and when its content reached values more than their solubility limit in zirconia, ZrTiO4 started to form in centre of zirconia grains. Formation of ZrTiO4 was found to be associated with monoclinic zirconia surrounded zirconium titanate grains, as confirmed by XRD patterns and BSE images. No traces of aluminium titanate peaks or any particular anisotropic alumina grains or in-situ fibres in SEM images were identified.

Keywords: Spark Plasma Sintering,Zirconia toughened alumina,Microstructure

59 - ABS 11

SYNTHESIS OF HIGH-ENTROPY ULTRA-HIGH TEMPERATURE CERAMICS

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As the name suggests, ultra-high temperature ceramics, UHTCs, are materials that can survive extremely high temperatures, although their ability to withstand rapid changes in temperature is much more limited. They can suffer from volume changes caused by phase transitions, particularly during oxidation since UHTCs are non-oxides. The use of additives in solid solution has been demonstrated to be able to modify the phases present in the resulting oxides and hence reduce or even eliminate the effect of the phase transitions. A natural extension to this is the creation of high-entropy UHTCs. These are thermodynamically stable solid solutions composed of five or more elements; this approach eliminates phase transitions by using thermodynamic principles. Several researchers have focused on using mixed binary transition metal borides or carbides to make monoclinic high-entropy UHTCs successfully by spark plasma sintering (SPS). This work is focused on producing high-entropy transition metal boride and/or carbide powders and then processing these into ceramics that will survive extreme conditions without phase changes or excessive oxidation.

The synthesis is based on the use of transition metal organic salts or halides as raw materials, i.e. sol-gel processing, followed by boro/carbothermal reduction; the goal is to limit the particle size to reduce processing temperatures and ensure that all the metal elements are homogeneously mixed at the atomic level. Therefore, the temperature and the fraction of boron carbide present must be controlled precisely and the boro/carbothermal reduction stage needs high vacuum to prevent oxidation. This paper will present the work achieved to date.

Keywords: UHTC, Boride, High entropy

60 - ABS 840

NANOMATERIALS FOR BIO-IMAGING, BASED ON RARE EARTH ELEMENTS DOPED HYDROXYAPATITE

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Currently, considerably preoccupation has been concentrated on the lanthanide (rare earth) elements for providing photoluminescent materials in bio-technological and/or electronic areas. The lanthanide ions are well-known for their photoluminescence properties in the visible and near-infrared regions, therefore they can be used in imaging of tissues or intracellular structures. For the applications in living cells it is fundamental to develop also biocompatible nanomaterials, thus obtaining a perfect biocompatible and biodegradable imaging probe based on nanoparticle still remains a challenging task [1-3].

In order to obtain biocompatible photoluminescent ceramic nanomaterials, the co-precipitation method was used. For this purpose, several attempts were made, to determine the optimal synthesis parameters. Therefore, a series of parameters varied, such as pH (7-11), the temperature at which the precipitation (40-100°C) takes place, the temperature at which the drying of the powders (70-150°C) occurs etc. Our studies have shown that different dimensions, morphology and modified (new, improved) physicochemical properties are obtained due to synthesis parameters variation. This systematic work made it possible to co-precipitate (at low temperature and low cost) new bio-ceramic photoluminescent materials at the nanoscale.

In this study, europium doped hydroxyapatite (HapE) was obtained by co-precipitation at low temperature. By doping with europium, hydroxyapatite acquires luminescent properties. Different Eu3+ concentrations were used (x_{Eu} = 0.005, 0.015 and 0.1), starting from calcium (calcium nitrate), europium (europium nitrate) and phosphorus (diammonium acid phosphate) salts. The Ca / P atomic ratio was 1.67 and the Eu / (Eu + Ca) atomic ratio ranged from 0 to 10%.

Morphological and structural characterization, as well as in vitro biological characterization were performed, using X-ray Diffraction, FT-IR, UV-Vis and RAMAN Spectroscopy, Scanning and Transmission Electron Microscopy.

Acknowledgment:

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Keywords: hydroxyapatite, europium, photoluminescent nanomaterials

61 - ABS 823

LARGE-PORE MESOPOROUS BIOACTIVE GLASSES FOR BONE GROWTH FACTOR ENCAPSULATION AND RELEASE

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Bone is a living tissue that continuously undergoes a dynamic process, known as bone remodeling, between bone resorption by means of osteoclasts (Oc) and new bone deposition by osteoblasts (Ob). During this process, the resorption of bone portions involves the excretion of enzymes that are able to digest the collagenous fibers [Silva et al., 2015] cause the release of the growth factors (GFs) stored in the bone matrix that in turn stimulate Ob migration and activity.

In this study, we aim to develop suitable bone GFs-carriers designed to re-balance incorrect exchange of biochemical signals between Ob and Oc which may occur in pathological condition (e.g. osteoporosis). The carriers will then be incorporated in the struts of a 3D printed biomimetic scaffold and the GFs should be gradually released in order to support bone regeneration.

Over the recent years, mesoporous bioactive glasses (MBGs) gained increasing interest in bone regeneration process due to their excellent bioactive and osteoconductive proprieties. However, these materials are characterized by nanopores not larger than 6-8 nm and thus unsuitable to host a large molecular weight molecule such as a GF [Barba et al., 2015].

To this purpose, MBGs with large pores were prepared using a tri-block copolymer F-127 as surfactant with the addition of 1,3,5-trimethyl benzene (TMB) as swelling agent and by varying the aging temperature from 100° to 200°C. During the unimer-to-micelle transition, TMB molecules penetrate into the hydrophobic core of the micelle, resulting in pore size expansion. Furthermore, the using of high aging temperature promoted the micelles crystallization of surfactant due to self-organization and expedite the polycondensation reaction, which lead to a higher surface area. Nitrogen physisorption analysis showed that were achieved pore dimensions of approximately 20nm for LP-MBGs, which are be about 30% larger than that of MBGs prepared through common sol-gel synthesis [Barba et al., 2015]. The nanoparticles were fully characterized by field emission scanning electron microscopy (FESEM), dynamic light scattering (DLS), x-ray diffraction (XRD), nitrogen physisorption analysis, wide-angle X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Horseradish peroxidase (HRP) was used as a model protein to evaluate the ability of the LP-MBGs to adsorb and release proteins. HRP amount in the release medium was evaluated by using a BCA protein assay.

The study is currently ongoing with bone GFs (e.g. insulin-like growth factor 1 -IGF1 and transforming growth factor Beta1 -TGFβ1). Western Blot analysis will be performed to evaluate GFs damages during the encapsulation process.

Acknowledgement

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 681798-BOOST) and by the Italian Minister of Research, Progetto FARE Ricerca in Italia (GRACE).

Keywords: Mesoporous bioactive glass, Bone tissue regeneration, Growth factor

62 - ABS 801

MULTIFUNCTIONAL SYSTEMS BASED ON HYDROXYAPATITE AND ANTITUMOR AGENTS FOR BONE CANCER TREATMENT

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The occurrence of cancer persists to increase. Bone metastases are considered to be a common cause for many types of malignant cancers and may occur as skeletal related events such as spinal cord compression, pathological fracture, hypercalcemia and definitely bone pain. The most common malignant metastases are in the lung and liver, the bone representing the third place in cases of malignant metastases so it is estimated that over 400,000 Americans manifest skeletal metastases annually [1].

Currently the most valid and chosen treatment options for bone cancer are chemotherapy, radiotherapy and surgery. In most cases, patients should have a combination of these three treatment methods for later observation of the effects [2].

This study investigates the activity of different antitumor agents in a material based on hydroxyapatite for the treatment of bone cancer. Hydroxyapatite, the main inorganic component of bones, along with collagen, the major organic part, design the first inorganic-organic natural composite material. At this point in time it is recommended to use natural materials, or as close as possible to natural materials for their applications in the biomedical field, in treatment of certain diseases, especially cancer.

In this study hydroxyapatite synthesis was performed under controlled conditions in order to obtain monodisperse, small nanoparticles and to avoid uncontrolled deposition of these nanoparticles in the forthcoming, starting from Ca(OH)2 and (NH4)2HPO4. The obtained dried precipitate was thermally treated at 600°C/3h, then suspended in various antitumor agent – specific solvent mixtures and homogenized until solvent evaporation. Morphological and structural characterization, as well as in vitro characterization were performed, using X-ray Diffraction, FT-IR, Scanning Electron Microscopy and specific antitumor tests.

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Keywords: hydroxyapatite, bone cancer, antitumor agent

63 - ABS 779

SYNTHESIS AND CHARACTERIZATION OF CALCIUM PHOSPHATE BIOCERAMICS POWDER THROUGH THE DISSOLUTION OF DJEBEL ONK PHOSPHATE ORE

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An Intense interest has been shown recently towards using calcium phosphate ceramics, as a substitute bone in dental and orthopaedic application. The most widely used calcium phosphate-based bioceramics are hydroxyapatite [HAP, Ca10 (PO4)6 (OH)2] and tricalcium phosphate [TCP, Ca3 (PO4)2], they all have the characteristic features of biomaterials, in particular, crystallographic similarity with natural bone minerals. The present study proved that, natural hydroxyapatite and tricalcium phosphate have been synthesized from natural phosphate of Djebel-Onk (Tebessa, East of Algeria) by following a dissolution precipitation method. The influence of temperature, ripening time, the pH value and the granulometry of the initial powder on the crystal growth of apatite was investigated. Different experimental techniques, including X-rays diffraction, SEM techniques, X-ray fluorescence and Fourier transform infrared analyses (FTIR) were used to understand chemical and structural characteristics of the synthesized powders. Through these results, we highlighted the possibility of preparing bioceramics of HAP and TCP from natural phosphate.

Keywords: Hydroxyapatite, Tricalcium phosphate, Phosphate ore

64 - ABS 770

FABRICATION OF MINERAL SCAFFOLDS FOR HARD TISSUE IMPLANTS: SYNTHESIS ROUTES

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The objective of the present paper is to design and synthesize new mineral scaffolds dedicated to hard tissue engineering applications by applying a polymer assisted method. The challenge is to respond to the current requirements imposed on bone implants: high mechanical properties, controlled morphology and personalized biological behavior.

In order to develop self-sustained porous architectures, calcium phosphates were deposited by wet chemistry approaches on bacterial cellulose membranes, resulting in hybrid materials that were lyophilized and then subjected to a thermal treatment. The mineral phase loading procedure was conducted by successive immersion in precursor solutions containing Ca2+ and [PO4]3- ions, under ultrasonic irradiation. The lyophilisation stage promoted the preservation of the 3D porous aspect specific to the polymeric membranes, while the calcination ensured the removal of the organic part and the consolidation of mineral scaffolds.

The samples were investigated from compositional, structural and morphological point of view through thermal analysis, X-ray diffraction, selected area electron diffraction, Fourier-transform infrared spectroscopy and scanning / transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy. The biological behaviour was assessed through in vitro tests: simulated body fluid immersion and stem cells assays concerning proliferation.

The influence of different processing parameters (type of precursors, number of immersing cycles, heating rate, calcination temperature and period) was evaluated in order to establish the optimized conditions of synthesis.

The final 3D porous architectures were based on different types of calcium phosphates: orthorhombic buchwaldite, hexagonal hydroxiapatite, as well as calcium pyrophosphate with tetragonal or orthorhombic structure.

Regarding the resulting morphology, it was tuned through the medium of the deposition and thermal parameters from spherical aggregates to a trabecular appearance.

Mineral scaffolds were prepared by a two step approach, namely wet chemistry deposition followed by calcination. Such biomaterials, prepared by a straightforward approach, represent important candidates for the development of bone scaffolds or bioactive fillers for bone cements.

Keywords: Mineral scaffolds, Polymer templates, Bioactivity

65 - ABS 767

THE QUATERNARY SYSTEM CaO-P_2O_5-ZnO-MgO AS A TOOL FOR DISCUSING THE EFFECT OF ZnO AND MgO ON THE PHASE STABILITY, DISSOLUTION AND BIOLOGICAL BEHAVIOUR OF DOPED TRICALCIUM PHOSPHATE MATERIALS

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The quaternary system CaO-P2O5-MgO-ZnO [1] is of great interest in the field of bioceramics due to the extensive use of Mg2+ and Zn2+ as doping agents, within non-toxic levels, to optimize the synthesis, microstructure, dissolution rate, bioactivity, biological performance in vitro and in vivo and osteogenesis of calcium phosphate based bioceramics such as tricalcium phosphate (TCP) and hydroxyapatite (HAP). [2-3]
The incorporation of these metal ions in solid solution in the structure of TCP or HAP, which do not break the biocompatibility have significant consequences on its behaviour. In the case of doped-TCP its biocompatibility is enhanced and also chemical stability is improved since transformation temperature of beta-alfaTCP is increased in more than 250° or 300°C as a function of Zn2+ and Mg2+ content.
Several studies can be found in the literature on the effect of Zn2+ or Mg2+ as doping agents on properties and behaviour of TCP (2-3), but only one has been found in the literature [4] taking into account the effect of both elements as a whole, and consequently, the information supplied by the quaternary system is essential for defining solid solution range, phase proportion, phase transitions and phases stability of these biomaterials.
Considering the information supplied by ZnO-CaO-P2O5 [5] and CaO-P2O5-MgO-ZnO diagrams and our previous results on the effect of ZnO additions on TCP bioceramics, pure TCP and ZnO/MgO TCP bioceramics have been synthesized by conventional solid state sintering reaction. The effect of ZnO/MgO content and sintering temperature on the beta/alfa stability, microstructure, dissolution rate "in vitro" in simulated body fluid (SBF) was discussed. Finally, the in vitro biocompatibility was also studied and discussed in cell culture test using MG-63 human osteoblast-like cells.

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5. Journal of American Ceramic Society 94 (7) 2011, 2213-2219

Keywords: P2O5-CaO-MgO-ZnO system, dopedTCP, biological behaviour

66 - ABS 741

EVOLUTION OF MICROSTRUCTURES AND MECHANICAL PROPERTIES IN HYDROXYAPATITE BIOCERAMICS BY SINTERING TEMPERATURE

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This work highlights effects of sintering temperature on microstructures, densification, grain sizes and boundaries, calcium/phosphorus (Ca/P) ion ratios, mechanical and bioactive properties in biocompatible hydroxyapatite (HA) ceramics prepared by the cold isostatic pressing process.

Hydroxyapatite (Ca10(PO4)6(OH)2, HA) biocompatible ceramics were prepared by using the cold isostatic pressing process and conventional solid-state-reaction sintering method. The pressed disks were sintered respectively at five different temperatures, i.e. 900, 1000, 1100, 1200 and 1300 oC for 2 hrs.

For density measurement of as-sintered specimens, Archimedes' method was used to determine the specimen's volume. The mechanical hardness of as-sintered ceramics was measured using the Vickers hardness tester. Structures of as-sintered HA specimens were characterized using X-ray diffractometer in a 2θ range of 10-80 degrees at a scan step of 0.05 degree. All experimental XRD patterns were analyzed employing Rietveld-refinement technique with the HighScore Plus software. The micro-Raman scattering spectra were acquired from as-sintered specimens at room temperature using a Raman spectrometer Nanoscale grain morphologies and structural space groups were investigated using a high-resolution TEM. To simulate potential loose of as-sintered HA ceramics in human body, the ion release studies were performed by immersing the ceramic specimens in 15 ml of Hank's balanced salt solution, which was placed in the atmosphere mixed with 5 % CO2 at 37 °C. Aliquots of the incubation solutions were collected for various durations of immersion, i.e. 1, 4, 7 and 14 days, and then were analyzed for the quantities of phosphorus (P) and calcium (Ca) ions using Inductively Coupled Plasma Optical Emission Spectrometry.

X-ray diffraction refinement analysis reveals that phase ratios of hexagonal HA phase and second phases are sensitive to sintering temperature. Grain sizes, densities and shrinkages of as-sintered HA ceramics increase with increasing sintering temperature. The Ca/P ratios of as-sintered HA specimens vary in the range of 1.63-1.71 for sintering temperatures of 900-1300 oC.

The specimen sintered at 1200 °C exhibits a maximal mechanical hardness due to a complete densification, smaller average grain size and less-flaw grain boundaries. XRD refinements and HRTEM images reveals that HA phase and impurities (TCP, TTCP and DCPD phases) are sensitive to sintering temperature. The deposition of calcium ions takes place in all as-sintered specimens after few-days immersion. Ion-release test indicates that phosphorus ions can be absorbed by as-sintered HA specimens in Hank's balanced salt solution. This study has demonstrated that optimal mechanical properties are sensitive to densification and grain structures.

Keywords: sintering temperature, grain size, ion release

67 - ABS 721

SOL-GEL DERIVED MINERAL SCAFFOLDS FOR HARD TISSUE APPLICATIONS

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The lack of bioactivity of metallic implants and the challenge of obtaining ceramic materials to respond to this property, but also to ensure the mechanical resistance imposed by applications in dental or orthopaedic fields, led to this project of designing and synthesizing mineral scaffolds.

The synthesis of mineral scaffolds started from a powder obtained through the sol-gel method, followed by a thermal treatments. The precursors used for the preparation of the precursor powder provided the hydrolysis and polycondensation reactions specific to this type of approach, resulting in the formation of a 3D network based on bridging oxygen bonds. To remove all gas generating components, a calcination was performed in optimized conditions. The calcined powder was homogenized with glucose, then shaped into cylindrical samples. In order to obtain the designed architectures, a thermal treatment was carried out, which led to the elimination of glucose and emergence of the desired porosity. The sintering was conducted so that the mechanical resistance of the ceramic material in the porous structure was also induced.

The samples were investigated from a compositional, structural, morphological and mechanical point of view by thermal analysis, X-ray diffraction, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy and compression strength measurements. From biological point of view, their behaviour was assessed in simulated body fluid and in the presence of stem cells.

The complex thermal analysis determined a calcination temperature of 600 °C. As major crystalline phase, akermanite was identified. The sintering in different conditions of temperature and period ensured the interconnection of the grains in a 3D network and the occurrence of a relatively uniform porosity in the entire volume. Also, good compression strength values were recorded for the obtained mineral scaffolds. The biological tests confirmed the bioactivity and biocompatibility of all samples.

Porous 3D structures were synthesized based on the sol-gel method combined with a thermal treatment at high temperatures. By adding glucose as sacrificial polymer, followed by its removal during sintering, microsized porosity and mechanical resistance were induced. This type of approach offers a very good perspective in the field of mineral scaffolds for dental and orthopaedic implants.

Keywords: Mineral scaffolds, Polymer templates, Bioactivity

68 - ABS 933

ELECTROPHORETIC DEPOSITION AND CHARACTERIZATION OF MULTIFUNCTIONAL HYBRID LAYERS ON NITI SHAPE MEMORY ALLOY

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In order to improve the biocompatibility of NiTi shape memory alloy and functionalize the surface, it was modified by formation of multifunctional ceramic hybrid layer consisted of titanium oxides, hydroxyapatite (HAp), and nanocomposite silicon dioxide/silver. It is known that calcium phosphate-based (CaP) layers, i.e. hydroxyapatite (HAp), facilitate the connection of a bone with a metallic implant [1]. Silica matrix enables incorporation of metal ions (e.g. silver) in low concentrations and their gradual release into the environment, which will provide a long-lasting antibacterial effect [2]. However, the greatest potential has composite materials, which combine multiple functions resulted from features of various materials.

In the work, an amorphous TiO2 interlayer, improving the corrosion resistance and an adhesion strength of ceramic particles to the metallic substrate [3], was produced on the NiTi substrate by autoclaving at 134°C for 30 minutes while the following hybrid coatings were deposited using electrophoresis (EPD). This method is an interesting alternative to many other methods of surface modification because of repeatability, mark off a low cost as well as a rapidity of the process [4]. First, SiO2/Ag nanocomposite was synthesized by a chemical reaction method and then the colloidal suspensions with different ratio of SiO2/Ag and HAp in ethanol/water were prepared for EPD. Electrophoresis was performed under different voltage (from 5 to 50 V) at time periods (from 0,5 to 5 minutes). Obtained homogeneous coatings were subjected to sintering at 800 °C for 2h. As a result of heat-treatment a crystallization of biocompatible titanium oxides and carbides was observed. The special attention was focused on a formation relatively thin, homogeneous and crack-free coatings able to deformation. The formed layers were characterized for morphology, topography, structure and bioactivity.

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Keywords: Hydroxyapatite, Ag/SiO2 nanocomposite, Surface modification

69 - ABS 207

INFLUENCE OF COLD PLASMA TREATMENT OF N_2, H_2 AND O_2 ON THE FORMATION OF CALCIUM PHOSPHATES ON THE SURFACE OF Al_2O_3/ZrO_2 NANOCOMPOSITES

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Owing to the bio-inert nature of the Al2O3/ZrO2 nanocomposite, surface coatings with calcium phosphates have been used to improve the interactions of the nanocomposites when implanted. The interaction between the formed phosphate layer and the nanocomposite surface may be improved by means of preliminary treatments [1]. Examples of such treatments include chemical treatments with acid and basic solutions and plasma treatments. The cold plasma treatment has been highlighted owing to its energy efficiency, as it reduces treatment time, and improves the adhesion and deposition of other materials. Furthermore, the treatment by cold plasma promotes changes in the surface chemical and physical properties without compromising the intrinsic properties of the biomaterial [2]. Thus, the objective of this study is to evaluate the influence of variation of different parameters such as plasma gas composition and pulse type in the formation of functional groups on the surface of Al2O3/5vol% ZrO2 nanocomposites. For this, samples of Al2O3/ZrO2 were conformed, calcined (400 oC / 1 h) and sintered (1500 oC / 2 h). In the surface treatments, gaseous compositions of N2, H2 and O2 with different percentages 10% N2, 50% H2, 40% O2 (1N5H4O), 20% N2, 50% H2, 30% O2 (2N5H3O), 30% N2, 50% H2, 20% O2 (3N5H2O), 40% N2, 50% H2, 10% O2 (4N5H1O) were used. The conditions used during the treatment were: gas flow (20 sccm), pressure (2 mbar), temperature (400 oC) and ton:toff ratio of the 100:50 and 50:100 s, referred to as pulse 1 and 2, respectively. Subsequently, the surfaces were coated with calcium phosphate. The treated and untreated surfaces before and after the deposition of the biomimetic coatings were characterised using optical emission spectroscopy, infrared spectroscopy, X-ray diffraction, and contact angle. In general, active species such as N2, N2+, O2, O2+, H, H, and OH were observed on the surfaces of the samples after the plasma treatments. The N2+ species presented higher intensity when compared to the other active species observed independent of the pulse used. The formation of active species on the surface of ceramic substrates promotes an increase in surface polarity, favoring the formation of hydrophilic groups. Another important characteristic observed was in relation to the contact angle. The treated surfaces had a lower angle when compared to untreated surfaces. In addition, previous cold plasma treatment contributed to a higher formation of calcium phosphates on the surface of nanocomposites. The calcium phosphate phases identified were: -TCP, -TCP and HA. Among the gas compositions used, the composition containing 1N5H4O (pulse 1) and 4N5H1O (pulse 2) favored the formation of calcium phosphates on the surface of nanocomposites. Thus, the previous surface treatment by plasma contributes effectively to a higher formation of calcium phosphates on the surface of the nanocomposites.μαβαβ

Keywords: Al2O3/ZrO2,surface treatment, plasma

70 - ABS 960

DESIGNING NANOSYSTEMS FOR BIOMEDICAL APPLICATIONS

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The increasingly resilient nature of bacterial biofilms towards antibacterial treatment has created a pressing need for an effective alternative.1 In this study, a novel therapeutic has been developed to meet this need through the simultaneous employment of both phototherapy and nitric oxide liberation within the same nanosystem. These nanosystems with phototherapeutic properties were designed with gold nanorods surrounded by a mesoporous silica nanoparticle shell. Subsequently, the surfaces of these nanoparticles were conjugated with a nitrosothiol group through a heat liable linker, enabling their stimulated release through infrared radiation to promote disintegration of the bacterial biofilm.2 The effects of these nanosystems were then analyzed through in-vitro assays of biofilms formed by Staphylococcus aureus (S. aureus, SA) cultures to study the synergetic efficacy of phototherapy and nitric oxide liberation. The transmission electron microscope (TEM) images shown below demonstrate the desired gold nanorod core situated within the mesoporous silica nanoparticle with a near spherical shape, an average diameter of 100 nm, and a pore morphology of radial symmetry. To functionalize the surfaces with the heat liable nitric oxide linker, an initial attachment of HS(CH2)3Si(OMe)3 to the mesoporous silica encrusted gold nanoparticles was performed prior to surfactant extraction to promote preferential adhesion to the exterior of the particles rather than within the pores.3 Afterwards, derivatization of the thiol group (-SH) into a nitrosothiol group (SNO) gave the R-SNO bond, which is sensible to the heat produced by the gold nanorods when stimulated with infrared radiation, producing in-situ release of NO.

Moreover, in vitro assays with biofilms of S. aureus demonstrated a synergistic effect of nanosystem exposure to IR radiation by the observed promotion of bacterial biofilm destruction. Confocal microscopy analysis at a scale of 20 µm illuminated significant deceased bacterial remains in red at the superficies of the biofilms in nanoparticle samples containing both the gold core and an NO functionalized linker. However, the residual appearance of live bacteria without the surrounding biofilm matrix indicates that the nanosystem design requires further optimization to meet the desired biological response. The synergetic design of mesoporous silica encrusted gold nanoparticles functionalized with a heat liable linker produced the elicited destructive effect on bacterial biofilms of S. aureus upon exposure to infrared radiation through the liberation of NO. These novel nanosystems have initiated a potent alternative for the treatment of bacterial infections.

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Keywords: mesoporous silica nanoparticle, hyperthermia, infection

71 - ABS 456

ATOMISTIC SIMULATION OF BETA-TRI CALCIUM PHOSPHATE A RESORBABLE BIOCERAMIC – CLARIFICATION OF CALCIUM PARTIAL OCCUPANCY AND STATIC DISORDER IN THE CRYSTAL STRUCTURE

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The limitations and potential complications correlated with autogenous bone grafts have created interest in the development of synthetic bone graft substitutes. β-tricalcium phosphate (β-TCP, Ca3(PO4)2) is one of the most promising materials for synthetic bone graft substitutes, because it is readily resorbed and replaced by new bone. However, even though the crystal structure of β-TCP was first published decades ago [1], it was recently found that the high symmetry of the published structure model over-simplifies some details of the atomic arrangements. Specifically, the Ca(4) sites are partially occupied and, while the occupancy was originally proposed as being fully disordered, such a structure is incommensurate with high quality X-ray diffraction analyses. It rather appears that there is some ordering of the Ca(4) sites, thereby lowering the symmetry of the trigonal structure, but in an arrangement that is not yet identified. The objective of this study is to investigate possible Ca(4) occupancy arrangements by using atomistic structure simulations to evaluate unit cells with different configurations of ordering.

Energy minimisation and molecular dynamics techniques were employed on all possible Ca(4) arrangements within the β-TCP unit cell. (3x3x1)-supercells, created by combining various arrangements of the different unit cells, were also explored with these computational techniques. Similar to other studies, the most energetically stable Ca(4) arrangement (lowest energy configuration, LEC) features the Ca atoms separated by the furthest distance. Studying various supercell arrangements, we find the stability of the structures depends on the configuration of the energetically disparate unit cells. Interestingly, some supercells that combine various energy configurations are substantially more stable than the supercell composed solely of LECs, suggesting longer range ordering or clustering could be important. Monte Carlo simulations on a larger sample size of supercell arrangements are therefore currently in progress to find the optimum structure. This optimum structure will then be compared to high quality X-ray diffraction data. Because the partially occupied Ca(4) sites allow for substitution of Ca for a variety of other (including mono- and trivalent) cations, understanding the nature of the Ca(4) disorder is crucial for determining dopant behaviour in the crystal lattice. For ongoing studies, simulating grain boundary segregation of doped and un-doped β-TCP will allow to clarify resorption mechanisms in vitro and in vivo.

[1] Dickens B. et al., J. Solid State Chem. 10, 232 (1974).

Keywords: beta-tricalcium phosphate

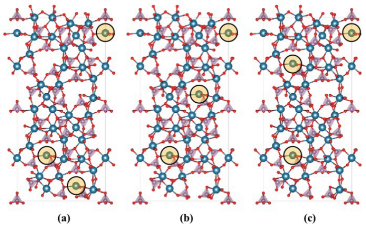
(a) (b) (c)

Figure 1. Ca(4) atoms are highlighted in yellow. The high energy structures (a) feature Ca atoms occupying sites closest together. The low energy structures (b) feature the Ca atoms placed the furthest apart. The intermediate energy structures (c) the Ca atoms placed neither close nor far.

72 - ABS 957

BIOMIMETIC AMORPHOUS CALCIUM PHOSPHATE

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Amorphous structures are more susceptible to inclusion of large quantities of various ions than crystalline ones. Current work presents development of synthesis of novel amorphous calcium phosphate (ACP) nanoparticles with biomimetic bone-like chemical composition.
Current synthesis of biomimetic ACP is based on recently developed wet chemistry method [1]. To incorporate necessary biomimetic elements into ACP various water-soluble salts were used.
Precipitation of ACP from ionically enriched solutions ensured obtaining of ACP with biomimetic bone-like composition. Possible crystallization of metastable ACP was hindered by the complex interplay of the many trace ions.

[1] J. Vecstaudza, J. Locs, J. Alloy. Compd., 700 (2016), 215-222.

Keywords: Amorphous calcium phosphate,Biomimetic composition,Nanoparticles

73 - ABS 416

ASIAN ELEMENTS ON MEISSEN PORCELAIN

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Meissen is a county in Dresden, Germany. In 1708, the first European mature porcelain was produced in Meissen Castle. In 1710, Meissen established the first royal porcelain factory. Since then, Meissen has become a center for European ceramic production. The formula of Meissen porcelain was first obtained from the French missionary Père Francois Xavier d'Entrecolles. He has been teaching in Jingdezhen(China's porcelain capital) for more than ten years. He has obtained a large number of Jingdezhen porcelain production methods and raw materials. After that, Père Francois Xavier d'Entrecolles sent the formula of Jingdezhen porcelain to a friend in France. Later, the Emperor Augustus received the letters from the French and tested it hundreds of times according to the formula written in the letter. Finally, in 1708, the mature European porcelain was created. In the following decades, Meissen porcelain influenced the production of porcelain in Austria, France, Italy, and the Czech Republic.

In the first 20 years of the production of Meissen porcelain, it was deeply influenced by Chinese and Japanese porcelain. For example, the classic onion pattern on Meissen porcelain is transformed from three fruit patterns in Chinese porcelain. The pattern of the characters on the Meissen porcelain is likely to come from the image of the Japanese. Moreover, the porcelain shape in Meissen porcelain has many similarities with traditional Chinese porcelain shapes. The gold color decoration on the Meissen porcelain has a close relationship with the gold color decoration on Japanese porcelain. This article compares the Meissen porcelain with Chinese porcelain and Japanese porcelain, and discovers the Asian elements from the Meissen porcelain, summarizing the connection between Meissen porcelain and Asian culture.

Keywords: Meissen Porcelain, Chinese Porcelain, Japanese Porcelain

74 - ABS 395

PREPARING TiO_2-DOPED BOROSILICATE FOAM GLASS COATED WITH HYDROXYAPATITE TO BE USED AS SCAFFOLDS

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This study verified the use of Borosilicate glass (BG) coming from unusable glass from the chemistry laboratory in the production of scaffolds to be used as implants and bone substituents, since BG presents good bioactivity and bioresorption [1]. With the purpose of improving the scaffold mechanical properties, 1% m/m TiO2 was added to the composition and to increase biocompatibility of the foam glass obtained, it was coated with hydrothermally synthesized hydroxyapatite. The unusable borosilicate glass was washed, dried, ground and sieved. Next, the composition of the powder obtained was verified using wavelength dispersive X-ray fluorescence. The foam glass was prepared from the mixture of BG powder, foam agent and TiO2 The mixture was homogenized, shaped and pressed. The resulting blocks were synthesized and characterized in relation to the physical properties (pore volume, apparent porosity, density and volumetric expansion). The value of volumetric expansion (%) was 174.742 ± 2.375 and of apparent porosity (%) 32.269 ± 1.175. The glass-ceramic coating with hydroxyapatite was carried out in autoclave. Ca and P precursors were added following the relation Ca/P=1,67. After 24h, the blocks were removed from the hydrothermal process, washed and dried. Optical microscopy analysis (OM) and Field emission scanning electron microscopy (FE-SEM) were carried out to verify the block HA coating. According to the OM analysis, the formation of pores of different sizes was seen, which were mostly considered macro and megapores. With the FE-SEM analysis, the HA formation on the whole surface of the material was verified, presenting needle-shaped crystals. The use of BG waste was seen to be promising for the production of foam glass to be used as scaffolds, due to the formation of open pores in its structure and the controlled expansion process.

Acknowledgements
CAPES, CNPq, Fundação Araucária, C-LABM

[1] *Hussain R. et al. Woodh. Pub. S. Biom., 2019,153-173.*

Keywords: Scaffolds,Biomaterial,Hydroxyapatite

75 - ABS 393

SYNTHESIS AND IN VITRO CHARACTERIZATION OF 3D MULTILAYER POROUS SCAFFOLDS

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Objetive The main objective is to obtain a 3D structure with interconnected porosity, high mitogenic potential and ability to stimulate cell proliferation for future applications in the regeneration of bone tissue. Scaffolds were constituted by a core of composition 3% $Ca2SiO4$ (C2S) / 97% $Ca3(PO4)2$ (TCP). In order to promote the cellular differentiation, the core was covered with outer layers of 85% C2S doped with different concentrations of ions Sr.

Materials & Methods The core of the scaffolds with composition 3% C2S was synthesized by sol-gel and polymer replicated methods. Polyurethane sponges were used as templates which were impregnated with mentioned solution and sintered at 950 °C during 8 h. Subsequently, the cores were impregnated with a new sol solution with composition 85% C2S doped with Sr ion in the following concentration: 0%, 1%, 3%, 25%, 50% and 100%. Finally, the scaffolds were sintered at 950 °C during 3 h. Bioactivity was estimated in vitro by different soaking times in Kokubo´s simulated body fluid (SBF) and characterized by SEM, XRD, FTIR and Hg porosimetry techniques.

Results Scaffolds multilayers were obtained by sol-gel and polymer replicated methods. Fig 1(a) show the microstructure of the scaffolds by SEM before soaking in SBF. This figure shows the typical morphology of the TCP in form of hexagons, coated by a layers of 85% C2S doped with 50% Sr. Besides, Fig 1(b) show the structure of the same scaffolds after 1 day soaking in SBF, showing the dissolution of the external layers and reveals that the core presents sticks of pyrophosphate. Additionally, by XRD and FTIR was identified the presence of the pyrophosphate phase in the core of the scaffolds. Only the samples with 1% and 3% Sr present in vitro bioactivity. This amount of Sr reduced the concentration of pyrophosphate, allowing the precipitation of hydroxyapatite.

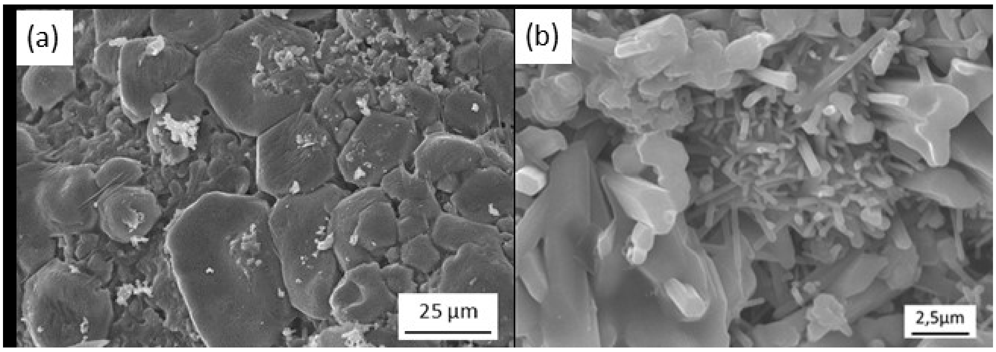

Fig. 1 - SEM micrograph of the scaffolds with the composition 3% C2S (core) / 85% C2S doped with 50% Sr (outer layers): (a) before and (b) after 1 day soaking in SBF.

Conclusions New 3D multilayer porous scaffolds were synthesized. By characterization was demonstrated the presence of pyrophosphate, phase that delays the in vitro precipitation of the hydroxyapatite on the surface of the samples. The presence of 1-3% Sr, reduced the concentration of pyrophosphate, allowing the precipitation of hydroxyapatite.

(1) H. Fleisch et al. Nature 212 (1966) 901-903.

Keywords: Sol-gel,Pyrophosphate,Multilayer

76 - ABS 338

BIOMIMETIC BIOCOMPOSITE BASED ON Zn^{2+} DOPED HYDROXYAPATITE FOR BONE TISSUE ENGINEERING

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Various kinds of metallic materials are used for clinical applications (especially as bone substitute materials) and still represent the best option for success, because of their acceptable biocompatibility and appropriate mechanical properties. After implantation, due to the mechanical, chemical and electrical activity of body fluids, the metallic biomaterials have a great tendency to corrode and release abrasive particles into the biological environments, usually causing inflammation and unwanted postsurgical interventions. Another issue regarding the usage of metallic implants is the lack of biological interaction (biological inertness), making the induction of osteogenesis processes or new bone ingrowth impossible [1-2].

The present work aims to address these limitations, by the developing a technological method for obtaining biomimetic inorganic-organic thin-film coated materials with biomedical applications. In order to achieve the desired goal, biocompatible composites were obtained and deposited using two deposition techniques: Spin Coating and MAPLE (Matrix Assisted Pulsed Laser Evaporation), resulting in a bioactive layer that could promote the osteointegration.

Collagen-calcium phosphates (hydroxyapatite) association mimics the natural bone tissue, while the substitution of Ca ions in the apatite structure with Zn ions accelerates the mineralization process. As it was expected, an advanced thin film homogeneity was assessed by MAPLE, being monitored by SEM and FTIR microscopy. Decreases of P-O and amide absorbance bands were observed as a consequence of introducing different Zn(2+) contents, explained by a variety of structural modifications of the apatite layer, that influence the confinement process towards the collagen template.

The in-vitro SBF assay emphasized the ability of the obtained coatings to stimulate the mineralization process as a result of synergic effects in the collagen-Zn(2+) substituted apatite association. For both deposition methods, the formation of spherical shapes associated to the growth of supplementary hydroxyapatite/calcium phosphates particles in the collagen matrix was reported, this statement confirming a prospective biomimetic behavior of the coatings to induce the mineralization.

Acknowledgment:
The support received from the national project “Innovative biomaterials for treatment and diagnosis” BIONANOINOV – P1, (PN-IIIP1-1.2-PCCD-I2017-0629) is highly acknowledged.

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[2] C. H. Jang, H. Lee, M. Kim, G. H. Kim, Accelerated osteointegration of the titanium-implant coated with biocomponents, collagen/hydroxyapatite/bone morphogenetic protein-2, for bone-anchored hearing aid, J. Ind. Eng. Chem., 63, 2018, 230-236.

Keywords: Bio-active layer,Calcium Phosphates,Collagen

77 - ABS 333

COMPOSITE SCAFFOLDS BASED ON CALCIUM PHOSPHATES AND BARIUM TITANATE FOR HARD TISSUE IMPLANTS

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Objective The objective of the present paper is the obtaining of new mineral 3D porous structures based on calcium phosphates and barium titanate dedicated to hard tissue engineering.

Materials And Methods The human bone presents in its dry form piezoelectric properties, which means that a mechanical stress results in electric polarization and an applied electric field causes strain. This electrical activity will affect many biochemical reactions in the body and promote bone repair and reconstruction conducive to fracture healing.

In order to obtain self-sustained porous architectures, calcium phosphates were deposited by wet chemistry reactions on bacterial cellulose membranes, resulting in precursor materials that were lyophilized and then thermally treated. Barium titanate nanoparticles obtained by the sol-gel method were loaded on the mineral scaffolds using the immersion technique at room temperature, followed by a second stage of thermal treatment.

The specimens were investigated from compositional, structural and morphological point of view by X-ray diffraction, Fourier-transform infrared spectroscopy, Raman spectroscopy and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy. The bioactivity was assessed through immersion in simulated body fluid.

Results The Fourier-transform infrared and Raman spectra confirmed the presence of barium titanate on the calcium phosphates based scaffolds. Moreover, the resulting morphology was provided by the SEM investigation; this feature was tuned through the medium of the deposition and thermal conditions.

The influence of the main processing parameters (nature of precursors, sequence and number of immersing cycles, heating rate, thermal treatment temperature and period) was assessed in order to establish the optimized synthesis route.

Conclusions In conclusion, barium titanate nanoparticles exhibit a good biocompatibility and osteoinductive properties when are deposited on 3D porous materials based on calcium phosphates. Such composites can be successfully used for tissue engineering applications.

Keywords: Composite scaffolds, Calcium phosphates, Barium titanate

78 - ABS 219

FABRICATION AND ENHANCED MECHANICAL PROPERTIES OF TRICALCIUM PHOSPHATE CERAMICS DOPED WITH ZnO AND ZnO-MgO BY SPARK PLASMA SINTERING

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At the present time, when developing calcium phosphate biomaterials for regenerative purposes for bone fixation and replacement, the main idea is to design a material capable of supporting the initial loads, transferring them progressively to the new bone, during its degradation. Also, these biomaterials must be replaced gradually by the new tissue, stimulating in turn the cellular response. This family of ceramics although could be considered the 'ideal' biomaterials due to its chemical composition, high biocompatibility and osseointegration [1] present the inconvenient of their limited mechanical properties [2, 3]. This fact restricts their use to areas where they are not required high mechanical performance, such as coatings on metal prostheses, composite materials and calcium phosphate cements.

In the present work we used the advanced method of unconventional sintering so-called Spark Plasma Sintering (SPS), which applies a pulsed electric current and a uniaxial mechanical pressure during the thermal cycle [4, 5] for obtaining high density ceramic materials. The main advantages of the SPS are a higher heating rate and lower sintering temperatures and residence times. This will allow controlling the microstructural development by obtaining high density materials with limited grain growth.

The sintering tests by SPS were carried out in the un-doped TCP and TCP doped with 1.0 ZnO and 1.0 ZnO-1.0 MgO (mol. %) compositions previously synthesized at 900 ºC/ 2 h. A sintering temperature of 1100 ° C/ 5 min was selected and a load of 50 MPa was applied automatically during the process. All the tests were carried out in a vacuum atmosphere of 4 MPa.

All samples were visually semitransparent and a complete physic-chemical characterization was made. Densification behavior were determined and compared with the samples obtained by conventional sintering (CS). Microstructural features of the sintered specimens were achieved by scanning electron microscopy-EDX. The dense bioceramics were also mechanically characterized, specifically the modulus of elasticity and Vickers microhardness were determined. These results were compared with the materials obtained by conventional sintering.

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Keywords: Tricalcium phosphate (TCP),Spark Plasma Sintering,ZnO, MgO

79 - ABS 215

SYNTHESIS AND CHARACTERIZATION OF CALCIUM PHOSPHATE BIOCERAMICS POWDER THROUGH THE DISSOLUTION OF DJEBEL ONK PHOSPHATE ORE

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An Intense interest has been shown recently towards using calcium phosphate ceramics, as a substitute bone in dental and orthopaedic application. The most widely used calcium phosphate-based bioceramics are hydroxyapatite [HAP, Ca10 (PO4)6 (OH)2] and tricalcium phosphate [TCP, Ca3 (PO4)2], they all have the characteristic features of biomaterials, in particular, crystallographic similarity with natural bone minerals. The present study proved that, natural hydroxyapatite and tricalcium phosphate have been synthesized from natural phosphate of Djebel-Onk (Tebessa, East of Algeria) by following a dissolution precipitation method. The influence of temperature, ripening time, the pH value and the granulometry of the initial powder on the crystal growth of apatite was investigated. Different experimental techniques, including X-rays diffraction, SEM techniques, X-ray fluorescence and Fourier transform infrared analyses (FTIR) were used to understand chemical and structural characteristics of the synthesized powders. Through these results, we highlighted the possibility of preparing bioceramics of HAP and TCP from natural phosphate.

Keywords: Hydroxyapatite, Tricalcium phosphate, Phosphate ore

80 - ABS 131

ELECTROSPUN GELATIN NANOFIBERS LOADED WITH MAGNETITE NANOPARTICLES AS BIOMIMETIC SCAFFOLDS FOR TISSUE REGENERATION

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The fabrication of extracellular matrix analogues (EMA) emerged in the last years as an appealing approach for tissue regeneration, mimicking architectural, microstructural and/or compositional features of the host tissue. Biomaterials with properties controlled at the nanoscale are essential to assist bone regeneration, and the use of modern technologies to generate 3D porous scaffolds attracts increasing interest. This study focused on the fabrication of electrospun nanofibrous scaffolds based on cold water fish skin gelatin (FG) loaded with magnetite nanoparticles.

The preparation of the electrospinning precursors was considered regarding the homogeneous distribution of the nanoparticles. Thus, 2-Hydroxypropyl β-cyclodextrin (CD) was used as dispersing agent and the ultra-sonication time was optimized. Both FG and CD were solubilized in magnetite nanoparticles with different nanoparticles concentrations (1% and 2% w/v). In order to obtain fibrous scaffolds, the multicomponent precursors were electrospun in controlled environment (25°C and 40% humidity). In order to further stabilize the fibers to prevent the dissolution in simulated body fluids, the synthesized fibers were crosslinked with ethanolic glutaraldehyde solution for 4 days, at room temperature. Forwards, the crosslinked meshes were extensively washed using ethanolic baths, and finally double distilled water.

Advanced morpho- and micro-structural characterization of the obtained fibrous scaffolds (before and after crosslinking) has been performed. The morphological and geometrical characteristics of the nanofibers, as well as the distribution of the nanoparticles into the scaffolds were determined by scanning electron microscopy (in ETD and BSED modes) and high resolution transmission electron microscopy (Fig. 1). In addition to HRTEM and SAED, X-ray diffraction was used to confirm the presence of the nanocrystalline phase. It could be observed that after crosslinking the morphology changes, a porous interconnected nanofibrous mesh is obtained (Fig. 1). The amount of dispersing agent influences the thickness of the fibers. When using CD the diameter of the fibers doubles when compared with the diameter of the fibers without CD.

To prove the potential application of the fibrous scaffolds for tissue regeneration, biocompatibility and cell adhesion in vitro studies with human adipose-derived stem cells were performed, presenting the potential of differentiation towards bone tissue.

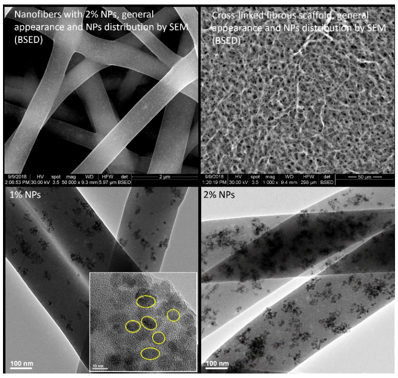

Fig.1. BSED SEM and TEM micrographs: upper panel left – homogeneous fibers and distribution of the NPs in the fibers and upper panel right – porous fibrous cross-linked mesh and homogeneous distribution of the NPs within the fibrous mesh (BSED); lower panels: TEM micrographs showing the homogeneously dispersed NPs in the nanofibers.

Keywords: magnetite nanoparticles, extracellular matrix analogues, tissue regeneration

81 - ABS 103

INFLUENCE OF HYDROTHERMAL TREATMENT ON STORED CHARGE DENSITY OF THERMALLY SPRAYED HYDROXYAPATITE

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Introduction: Hydroxyapatite (HAp) coatings on metallic substrates have been broadly used as orthopaedic implants at load bearing sites. In the last decades attention has been directed to the ability of HAp to create electrically charged surface by polarization in an electric field [1-2]. Studies have shown that a charged surface enhances formation of apatite layer [1] and bone cells [2]. One of the challenges in producing HAp coatings is the loss of hydroxyl (OH) ions during the thermal spray process [3]. Therefore, additional processing such as hydrothermal treatment (HT) could be used to return OH ions back into the structure. In this work the effect of the amount of OH ions on the stored charge density of thermally sprayed hydroxyapatite was studied.

Experimental: HAp spray powder (CamBioceramics) was flame sprayed onto grade 1 titanium substrates (d=12mm). Thickness of HAp coatings was about 50±10μm. Coatings were hydrothermally treated (HT) in water vapour at 250°C for 12h to restore OH ions in the HAp structure. The OH ion content was determined from FTIR spectra after deconvolution of the spectral region at 500 - 700 cm-^{1} with MagicPlot Student software. Electrical polarization was performed with platinum electrodes in an electrical furnace. Polarization was conducted at 400 °C in a d.c. electrical field of 20 kV/c for 1 h and then cooled to room temperature while maintaining the electrical field. Thermally stimulated depolarization current (TSDC) measurements were carried out in air from RT to 850 °C at a heating rate of 5°C/min. The polarization charge was calculated from the TSDC curves.

Results: The OH ion content calculations from FTIR spectra in spectral region 500-700 cm-^{1} showed an increase from 23±2% for as-sprayed coatings tio 61±3% for HT treated coating (see Fig.1a). The maximum charge density, determined from the TSDC curves, was 5.8 μC/cm^{2} for HT treated and polarized coating, while no charge density was determined for untreated coating (see Fig.1b).

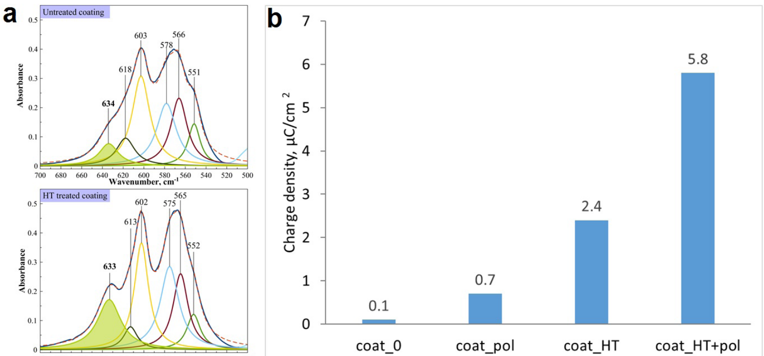

Fig. 1. Spectral deconvolution of FTIR spectra for coatings before and after HT treatment (a). Comparison of charge densities for coatings with different pre-treatment (b).

Conclusions: Stored charge capacity in HAp coatings increased from 0.1 till 5.8 μC/cm^{2} by improving OH ion content. Therefore, it could be concluded that OH ion content is an important contributor to the generation of surface charge.

Acknowledgement: This work has been supported by the EC 7th Framework Program MERA.NET project “Implants signal to bone for bone growth and attachment” Nr. ESRTD/2017/4.

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Keywords: Hydroxyapatite coatnings,Polarization,Surface charge

82 - ABS 74

NOVEL SMART AND RESORBABLE DEVICES TO TREAT OSTEOPOROTIC FRACTURES: THE CHALLENGE OF THE GIOTTO PROJECT

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Osteoporosis (OP) is a worldwide disease, defined in 2001 as "a skeletal disorder characterised by compromised bone strength predisposing a person to an increased risk of fracture" by the National Institutes of Health. Till the beginning of the new millennium this epidemic, progressive disease has been under diagnosed and underestimated until a call for action was launched in 2001 by the International Osteoporosis Foundation (IOF) to be active on policy issues focused on preventing and managing this bone-fragility disease. Nowadays, in the EU, one of us experiences an osteoporotic fracture every 30 seconds and with the current demographic shift the incidence is expected to double in few decades. OP has been for long time identified as a women-only disease and still is by the lay public, but recent data shows that it affects 1 out of 2-3 women and 1 out of 5 men above fifty years, and that the prognosis for men is often significantly worse. Appropriate anti-osteoporotic drugs are available but have serious side effects and they do not promote fracture healing. The H2020 GIOTTO project aims to face this osseous, degenerative pathology through an innovative, smart and personalised approach.

As OP can lead to different types of fractures located in dissimilar body parts, the GIOTTO project will develop different medical devices designed to treat specific osteoporotic fractures.

In particular, three different solutions will be designed and developed:

1) 3D bioresorbable graded scaffold, which can be fixated with screws, to treat long bone fractures
2) Bioactive and bioresorbable electrospun collagen scaffolds to deal with pelvic fractures;
3) Bioresorbable and injectable calcium sulphate composite cements to stabilise vertebral fractures and to promote bone regeneration.

The three composite devices will contain smart nano-biomaterials (mesoporous glass particles and ion doped nano-hydroxyapatites) able to release chemical and biological cues to stimulate bone regeneration while reducing bone loss. In particular, an active molecule (ICOS-Fc) able to inhibit osteoclast activity will be used in synergistic combination with the smart nanobiomaterials. Nanofunctionalisation and the smart release of active molecules will allow for the systematic cell recruitment and activation needed to face the challenges of stimulating bone tissue regeneration in the elderly. The use of 3D printing and direct-writing electrospinning will enable device personalisation to match and better align with the patient's anatomy and fracture type. A further boost to bone regeneration will be provided by the activation of cellular mechanotransduction, using functionalised magnetic nanoparticles and an external oscillating magnetic field.

Acknowledgments

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www.giottoproject.eu

Keywords: Mesoporous glass, Surface functionalisation, Osteoporosis

83 - ABS 72

CERAMICS COMPOSITES BASED ON HYDROXYAPATITE AND CALCIUM ALUMINA PHASE

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Bioceramic composite materials based on apatite minerals are commonly used for bone tissue replacement. Controlling of the additives and porous structure can increase bioactive properties and improve the mechanical resistance of the final bone scaffolds. Generally, these aspects are important criteria in tissue engineering. The apatite bioactive substance can be used as a single phase material or as a matrix of a composite specia. Although the on-going research is focused on using a combination of inorganic matrix with biodegradable polymeric substances including PLA, chitosan or PCL, the inorganic reinforcement based on newly formed phases between apatite and calcium aluminates are not fully studied. In this work the influence of interaction between calcium aluminates and hydroxyapatite on the final properties of the scaffolds was studied. Calcium aluminate, tricalcium aluminate and calcium hexaaluminate phases were mixed with pre-synthesized hydroxypatite (D50 = 6,26 μm) in various concentrations (10, 5, 1 wt. %). The aqueous suspension (solid to water concentration - 50 – 60 wt. %) was prepared from the mixture by intensive stirring (1 000 rpm). Into homogenous suspension the foaming agent (Schäumungsmittel Flüsig W 53) was added and the in situ foaming process was occurred. Foamed suspension was moulded to Al mould with dimensions 10x10x10 mm. An optimal drying and sintering conditions of foamed samples were determined by heating microscopy and TG-DTA analysis. The phase composition and microstructure of the sintered scaffolds was observed by X-Ray diffraction analysis and scanning electron microscopy, resp. The ability to create a new phase on scaffold surface was tested in vitro by immersion of the samples in the simulated body fluid liquid (Kokubo´s composition). The treated scaffold samples were examined by SEM analysis after 1, 3, 7, 21 and 28 days of immersion to observe the formation of a new phase layer. Simultaneously with the surface monitoring the concentration of important ions (i.e. Ca, P, Al) in the applied SBF solutions was determined.

Keywords: Hydroxyapatite, Bioceramics composite, CA phase

84 - ABS 70

Ca^{2+} AND Mg^{2+} TANDEM INFLUENCE ON PHASE TRANSFORMATION, SINTERING AND CHEMICAL STABILITY IN ARTIFICIAL SALIVA OF ZIRCONIA - ALUMINA BIOCERAMIC

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Alumina and zirconia-based ceramics present reduced wear rates and excellent long-term biocompatibility, which can increase the longevity of the implants.

In this study, the effects of simultaneous admixture of CaO and MgO on the crystalline phases, crystallite sizes and sintering properties of coprecipitated ZrO2 -Al2O3 powder are investigated using complex thermal analysis (TG, DTA, DTG), X-ray diffractometry (XRD), scanning electron microscopy (SEM) coupled with EDS.

Correlations among composition - microstructure and properties of the coprecipitated Al2O3-ZrO2 powder after sintering at 1050oC, 1350oC and 1500oC with 2 hours soaking time at each temperature were performed.

The results showed that development of tetragonal and cubic phase of zirconia stabilized with Ca2+ and Mg2+ was effective at 1350oC and 1500oC respectively.

In dental applications, dental materials are soaked in saliva, which contains a large number of ions which in turn may accelerate the corrosion of materials. In such context, the chemical stability in modified Fusayama-Meyer type artificial saliva of sintered alumina – zirconia ceramics was also investigated.

The ceramic samples sintered at 1500oC show a better chemical stability, as the pH variation is lower when using a starting immersion solution with pH = 7.4. However, the variation of pH after immersion in artificial saliva is obvious after 216-288 hours due to the ionic transport between bioceramic and the solution.

Keywords: bioceramic,zirconia,alumina

85 - ABS 826

THERMOELECTRIC PROPERTIES AND PHASE EQUILIBRIA IN CERIA DOPED $Ca_3Co_4O_9$ CERAMICS

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Due to the increasing population and energy consumption of the world, to find new types of clean and renewable energy resources has become more urgent. However, large amount of energy is being lost in industrial processes as waste heat. Thermoelectric materials and devices are considered a promising possibility to convert energy between heat and electricity. However, thermoelectric devices are not commonly used because of their low efficiency, relatively high cost and material toxicity. The Ca3Co4O9 system has attracted great attention in thermoelectric application due to high efficiency and lack of toxicity. Recent experimental works showed that the thermoelectric performance of calcium cobaltite can be improved by metal oxide doping such as alkaline and alkaline-earth metal oxides. However, there are limited studies on the effect of rare-earth oxides on the thermoelectric properties and thermodynamic properties. In the present work, systematically the rare-earth solubility in Ca3Co4O9 has been investigated and effects of dopant concentrations on thermoelectric properties were studied. A direct relation between the ionic radius and solubility has been determined. An isothermal section in the CaO-CeO2-CoO phase diagram has been constructed.

Keywords: Thermoelectric Effect, Phase Diagram, Rare Earth Dopant

86 - ABS 970

ASSESSING CONDUCTION AND DIFFUSION BEHAVIOUR OF ALKALI IONS IN CALCIUM SILICATE GLASSES

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In CIGS and CZTS based thin film solar cells, the performance of the devices is improved with the out-diffusion of Na from soda lime glass substrate to the absorber layer. The Na reportedly passivate the grain boundaries of the absorber layers that prevent recombinations of electrons & holes at the grain boundaries. In this work, we present a comparative study of the synthesized different alkali oxide containing glasses with commercially available SLG substrate. The dielectric, conductivity and diffusivity of glasses are characterized using impedance spectroscopy. Thin layers of Mo, which are traditionally used as bottom electrode in CIGS and CZTS based solar cells, were grown by DC magnetron sputtering on the synthesized glasses and the diffusion kinetics of alkali ions from substrate to the overlayer was assessed using secondary ion mass spectroscopy. Substantial amount of diffusion of alkali ions is observed, which is expected to affect the performance of thin film solar cell.

Keywords: Glass, substrate, SIMS

87 - ABS 969

DEPOSITION TIME EFFECT ON CZTS THIN FILMS PROPERTIES FOR PHOTOVOLTAIC APPLICATION

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In this work, the effect of deposition time on CZTS thin film properties was investigated. The XRD patterns confirmed the formation of tetragonal CZTS thin films with a preferential orientation along (112) direction, the Raman spectroscopy shows an intense Raman peak position at 335 cm-1 which assigned to CZTS material. While, the optical properties show a high absorption coefficient and an optimal band gap energy which decreases from 1.6 to 1.3 eV as the deposition time increase from 15 and 45 min. the p-type conductivity of CZTS material was confirmed, whereas the carrier concentration was in the order of 1018 cm-3 and the conductivity increase from 7 to 124 (cm) as the deposition time increase.

Keywords: CZTS, Spray pyrolysis, solar cells

88 - ABS 748

EXPERIMENTAL PHASE STUDIES IN THE La-X-Ni-O (X=Mg, Ca, Sr) SYSTEM

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The lanthanum nickelates have been considered as a potential cathode material for intermediate temperature solid oxide fuel cell applications. In recent works it is reported that the performance of nickelate type cathodes can be improved by SrO and CaO doping. However, there is no detailed literature information on phase equilibria of the La2O3-XO-NiO (X=Mg, Ca, Sr) ternary oxide system. In order to build chemically stable fuel cells, not only the thermodynamic stability of the electrolyte and electrodes themselves, but also the reactivity between component materials should be well established. The work aimed to investigate ternary phase equilibria of the cathode itself and also compatibility/reactivity between the cathode and LSGM electrolyte. The experimental work has been designed based on the calculated phase diagrams. In the La-Sr-Ni-O system, extended solid solutions (La,Sr)2NiO4 was found. However, in the Ca and Mg containing systems limited solubility limits were determined. Also chemical potential diagrams of the system simulation fabricating and operation conditions were calculated.

Keywords: LSGM, Ceria, Calphad

89 - ABS 743

PHOTOCATALYTIC PROPERTIES OF CERIA/POLYANILINE HETEROSTRUCTURED POWDER

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With the development of industry and the rise of environmental awareness in the past decade, photocatalyst, one of the most potential and environmentally friendly materials, has attracted increasing R&D attention for the wastewater treatment applications. Cerium dioxide (CeO2, ceria), a catalytic material with good thermal stability, can be used as a photocatalyst to photocatalytically degrade organics under the ultraviolet (UV) irradiation (about 5% of solar energy). However, the efficiency of electron-hole pair separation is low under sunlight irradiation, and thus the application of the CeO2 photocatalyst is limited. In this study, a nanosized CeO2 powder was prepared by precipitation method; and subsequently, various amounts of polyaniline (PANI) nanoparticles were deposited onto the surface of CeO2 nanoparticles by polymerization method. The photocatalytic activity of the CeO2/PANI heterostructured powders by photodegradation of methyl orange (MO) under visible light irradiation. Experimental results demonstrated that the heterostructured powder at a CeO2/PANI ratio of 10/1 exhibited the highest photocatalytic activity in a degradation rate of 81% within 4 h under visible light irradiation. This can be attributed to the formation of a heterostructure, so-called p-n junction, at the interface between n-type CeO2 and p-type PANI, causing a reduction in band gap energy. Furthermore, UV-Visible and photoluminescence (PL) spectroscopies indicated that the visible light absorption and electron-hole pair separation of CeO2 can be enhanced by the addition of PANI. The effects of material characteristics on the photocatalytic properties were investigated and discussed.

Keywords: cerium dioxide, polyaniline, heterostructured powder

90 - ABS 742

ENHANCED PHOTOCATALYTIC CO_2 REDUCTION ACTIVITY USING HETEROSTRUCTURED CHALCOGENIDE COMPOSITE PHOTOCATALYST

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A new heterostructure consisting of Ru and Cu co-doped ZnS nanoparticles anchored onto a MoS2-graphene hybrid (RCZS/MSG) was synthesized by microwave assisted solvothermal method. Using a facile two-step method, RCZS nanoparticles were in situ grown on the surface of MSG hybrid, which generated high density of nanoscale interfacial contact between RCZS and MSG hybrid. Therefore, the photo-excited electrons of RCZS can be readily transported to MoS2 through graphene backbone, thus reducing the electron-hole pair recombination. Since Ru and Cu co-doped ZnS is anchored onto a MoS2-graphene hybrid, the intensity of PL emission of the chalcogenide composite photocatalyst obviously decreases. In addition, a quaternary ruthenium and copper-based chalcogenide RCZS has shown a number of advantages in harvesting the solar energy. With increasing the concentrations of Ru up to 4 mol%, the band gap could significantly decrease from 3.52 to 2.73 eV. At the same time, we also analyzed the charge-transfer resistance of the as-synthesized chalcogenide composite photocatalysts to further investigate the electrochemical impedance characteristics. The charge transfer resistance was found to decrease from 38.0 to 12.7 ohm with increasing of ruthenium doping content, where chalcogenide composite photocatalyst would enhance the charge transfer and result in the effective charge separation. Additionally, the photocatalytic activity of as-synthesized chalcogenide composite photocatalysts was evaluated by the photocatalytic carbon dioxide reduction using simulated sunlight irradiation. Optimized photocatalytic conditions for the highest carbon dioxide reduction have been investigated, considering the factors such as the concentration of NaOH solution, the amount of RCZS/MSG photocatalyst, and the content of co-doped ruthenium. The results of photocatalytic activity were presented that the doping of ruthenium could further enhance this activity. The optimal content of Ru dopant was about 0.5 mol% and the corresponding methane gas production rate was 58.6X10-6 mol h-1 g-1 in the presence of 2 M NaOH solution as an electron and proton donor using 0.05 g L-1 of photocatalyst.

Keywords: zinc sulfide,MoS2-graphene hybrid,photocatalytic CO2 reduction

91 - ABS 736

SYNTHESIS AND CHARACTERIZATION OF $LaNi_{1-x}Cr_xO_{3-\delta}$ FOR USE IN FUEL CELLS

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The current generation of energy based on fossil fuels has led to a worsening of the greenhouse effect. In this context, several clean and renewable energy sources have been studied. Among these sources, the fuel cell has been highlighted because they are devices that convert chemical energy directly into electrical energy. Among the various types of fuel cells, the solid oxide fuel cell has the highest power generation, however, high operating temperatures lead to high production and operation costs. In these cells the challenge is to find materials that allow the lowering of operating temperatures. In this sense, the objective of this work was to study the synthesis and characterization of LaNi(1-x)CrxO(3-d) (with x from 0 to 0.7) for use in fuel cell cathodes. All compositions were synthesized using the modified Pechini method. Calcination was performed in the air at 900°C for 4 hours. After obtaining the powder, they were characterized by X-ray diffraction and Scanning Electron Microscopy. The specimens were pressed and sintered at temperatures between 1300°C and 1600°C for 4h. The characterization of the specimens was performed by X-ray diffraction with Rietiveld method, scanning electron microscopy with EDS, apparent porosity and apparent density measurements, and Impedance Spectroscopy. The refinement results of the X-ray diffraction spectra showed only one phase formed in all the compositions studied. The increase in Cr amount led to an increase in porosity. The spectroscopy measurements showed that the compositions presented an electronic conductivity, and the composition with x = 0.5 obtained the highest values of conductivity, showing potential to be used as a cathode of fuel cells.

Keywords: SOFC, Electrode, Electrical Conductivity

92 - ABS 971

TUNING MASS DIFFUSION IN CERIA SHAPED NANOCRYSTALS

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Solid state diffusion (SSD) controls the way oxides get structured from the atomic to the macro scale, assembling microstructures and shapes that define properties and functionalities. In this study, we show how surface energy at the 10 mol% Gd-doped CeO2 (GDC) nanometric crystals with different morphologies, i.e. nanocubes (NC), nanorods (NR) and random nanoparticles, can control the mass diffusion mechanisms leading to extremely different microstructural assembling, ranging from rapid densification to stable pore formation. Such oxide is relevant in several chemical, environmental and energy technologies in which different microstructures, either porous, for high catalytic activity, or as dense membranes, with preferably low sintering temperatures, are required. A hydrothermal synthesis method allowed to obtain single phase GDC as NCs and NRs with narrow particle size distribution. The NR and NC samples are pressed in the green form with relative density of ~50% and 40%, respectively. Dilatometric analyses revealed that the NRs show the fastest densification starting at relatively low temperatures of ~300 °C, whereas NCs exhibit no densification during the thermal treatment. Scanning electron microscopy analyses of sintered samples confirmed nearly full densification of the NR. On the other hand, rounded shape grains of NC indicate an intense diffusive process that promotes the change from the cubes to the spherical while keeping an extensive porosity in the consolidated ceramic body. The different morphologies indicate that topological factors in nano ceria appear effective in tuning the microstructural assembling, with the potential of tuning microstructures from highly dense microstructures at low temperatures to stable porosity at high temperatures.

93 - ABS 685

EXPERIMENTAL PHASE STUDIES AND THERMOELECTRIC PROPERTIES IN DOPED $Ca_3Co_4O_9$ CERAMICS

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Thermoelectric materials have drawn great attention for decades, due to direct conversion between thermal and electrical energy, thus providing an alternative for power generation and refrigeration. Despite this potential, thermoelectric devices are not in common use because of their low efficiency, relatively high cost and material toxicity. The Ca3Co4O9 system has attracted great attention in thermoelectric application due to high thermal stability, efficiency and lack of toxicity. The Ca3Co4O9 compound is a misfit-layered oxide consisting of two monoclinic subsystems, namely the Ca2CoO3 layer and the CoO2 layer. It does not only exhibit surprising thermoelectric properties due to a large thermopower, but also has low electrical resistivity and good thermal stability up to 800°C which makes the compound an ideal material for high temperature thermoelectric applications. Recent experimental works showed that the performance of calcium cobaltite (Ca3Co4O9) can be improved by metal oxide doping such as alkaline and alkaline-earth metal oxides. For the practical use of these materials not only the concentration-performance relation but also the phase equilibria and thermodynamics of systems are needed. However, literature data on phase diagrams in the cobaltites is very limited. Therefore, in the present work ternary phase equilibria in the CaO-XO-CoO oxide system (X=Na, Ba) has been experimentally investigated and isothermal section were constructed. Electrical resistivity, thermal conductivity and Seebeck coefficient of the samples were measured upto 800°C.

Keywords: Cobaltites, Phase Equilibria, Metal Oxides

94 - ABS 636

PREPARATION AND CHARACTERIZATION OF SOLID ELECTROLYTE COMPOUNDS CONSISTING OF DOPED LANTHANUM GALLATE AND YTTRIA STABILIZED ZIRCONIA

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Strontium- and magnesium- doped lanthanum gallates have attracted great attention in recent years due to their high ionic conductivity, about twice that of yttria stabilized zirconia, and possible application in intermediate temperature solid oxide fuel cells. In this work, the ionic conductivity, hardness and microstructure of compound solid electrolytes consisting of doped lanthanum gallate and yttria stabilized zirconia were investigated aiming to improve the overall performance of this ceramic material.

La0.9Sr0.1Ga0.8Mg0.2O3-δ was prepared by the mixed oxide method, commercial yttria stabilized zirconia being introduced in the ratios of 1, 10 and 20 wt.%. The sintering of green compacts was performed at 1450°C for 4 h. Characterization of sintered samples were carried out by density measurement, X-ray diffraction, scanning electron microscopy, impedance spectroscopy and Vickers hardness.

The relative density increases with increasing amounts of yttria stabilized zirconia achieving ~99% with 10 wt.% addition. X-ray diffraction patterns exhibit the characteristic orthorhombic structure of doped lanthanum gallate as the major phase. The average grain size and the hardness also increase with increasing the content of the additive electrolyte. The highest ionic conductivity was obtained for samples with 1wt.% of yttria stabilized zirconia.

The compound solid electrolyte shows enhanced properties compared to the parent doped lanthanum gallate. Its properties may be tuned with suitable choice of the additive content.

Keywords: lanthanum gallate, microstructure, ionic conductivity

95 - ABS 553

IMPROVED PHOTOCATALYTIC HYDROGEN EVOLUTION OF ZINC SULFIDE WITH METAL ION MODIFICATION VIA A MICROWAVE-ASSISTED SOLVOTHERMAL METHOD

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Copper doped ZnS and Ru, Cu co-doped ZnS nanospheres were successfully synthesized in DI water and ethanol solvent by a microwave-assisted solvothermal method using citric acid surfactants in aqueous medium. Surfactants could tune the CB edge position to become more negative than hydrogen production level (E = –0.43 eV, H2/H+). 2CuZnS with CIT has the highest activity (2,961.1 μmol h–1 g–1) for hydrogen evolution. Dopants act as an electron sink that diminishes the electron/hole pair recombination, resulting in a further improvement for the photocatalytic activity. Cu-doping into the lattice or interstitial of ZnS has provided suitable impurity energy levels, which make it easier for the excited electrons from the valence band of ZnS injecting into the conduction band of ZnS. Copper doped ZnS, such as 4CuZnS photocatalys, had the maximum yield of 3,717.8 μmol h–1 g–1 for hydrogen evolution from an aqueous solution containing 0.1 M Na2S at pH 3 and 0.15 g L-1. For Ru, Cu co-doped ZnS nanospheres, Ru3+ ion makes its own energy level as the center for recombination of excited carriers. Therefore, ruthenium co-doped CuZnS photocatalysts seems to loose the activity to enhance the photocatalytic hydrogen evolution.

Keywords: zinc sulfide,co-doped,hydrogen evolution

96 - ABS 444

ENHANCING THE SINTERING PROPERTIES AND IMPROVING MICROSTRUCTURE OF GADOLINIUM-DOPED-CERIA INTERLAYER AT A LOWER TEMPERATURE BY DOPING WITH TRANSITION METAL ELEMENTS FOR SOFC APPLICATION

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A dense CGO ($Ce_{0.9}Gd_{0.1}O_{2-x}$) interlayer is an essential component between zirconia-based electrolytes and cathodes (e.g. $La_{0.60}Sr_{0.40}Co_{0.20}Fe_{0.80}O_{3-x}$ (LSCF)) to inhibit the interfacial elemental diffusion and formation of unwanted insulating phases such as $SrZrO_3$. Inherently, CGO has a high sintering temperature (~ 1400 °C), which results in the formation of more resistive (Zr, Ce)O_2 based solid solutions at the electrolyte/CGO interface. In this study, the effect of transition metal (TM) elements (Co, Cu, Fe, Mn, & Zn) doping on the crystal structure, densification, and microstructure of CGO is studied. The TM-doped CGO powders were synthesized by a sol-gel based Pechini method. TM-doped CGO powders showed a slight reduction in lattice parameter as observed in XRD patterns. Dilatometry data indicated that the TM-doping in CGO do wonders and reduce the necking temperature by up to 600 °C. This played an instrumental role in densifying the CGO interlayer at a temperature as low as 1100 °C. Scanning electron micrographs of TM-doped CGOs sintered at 1100 °C showed dense microstructures with the negligible amount of open pores. TM- doped CGO interlayers, fabricated by a simple screen printing method and sintered at a temperature of 1100 °C, were also observed by SEM for their microstructures and adhesion with electrolyte. The TM appeared to have improved the densification in the order of Zn < Fe < Co < Cu < Mn. Arrhenius plots showed that the total conductivities of TM-doped CGO were also slightly increased.

Keywords: SOFC, CGO, sintering

98 - ABS 225

REDOX STABILITY OF ALTERNATIVE CERAMIC COMPOSITIONS FOR SOLID OXIDE FUEL CELL ANODES

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Solid-oxide fuel cells (SOFCs) typically undergo unwanted redox cycles during operation and this causes dimensional instability for the anode electrode. The state-of-the-art Ni/YSZ anode experiences a linear expansion of up to 1% when oxidized causing an irreversible microstructural change. This study focused on the evaluation of redox stability for various scheelite, double-perovskite, and rutile materials by controlled-atmosphere dilatometry.

All compositions evaluated in this study were prepared by solid-state synthesis. The phase purity was confirmed by X-ray diffraction. The potential anode samples were subjected to two ten hour long redox cycles in air and forming gas at 800 degrees Celcius. The linear expansion at isothermal conditions was compared to common electrode and electrolyte, such as yttrium-stabilized zirconia (YSZ) and strontium-doped lanthanum titanate (LST). For example, it was found that 38% porous LST experienced a reversible linear expansion of 0.013% at 800 degrees Celcius. The electrical performance was also measured by four-point DC conductivity. The redox performance of other non-traditional compositions with various doping strategy will also be discussed in this poster.

Keywords: Anode, Thermal expansion, Electrical conductivity

99 - ABS 947

SURFACE MODIFIED Ce(Mn,Fe)O_2 / La(Sr)Fe(Mn)O_3 AS CERAMIC ANODE FOR DIRECT-HYDROCARBON FUEL SOLID OXIDE FUEL CELLS

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Direct utilization of hydrocarbon or bio fuel is one of the emerged important issues in Solid Oxide Fuel Cells. (SOFCs) development because of high energy conversion efficiencies and simple operation mode of the systems. However, the use of high carbon contents fuels directly has been limited due to several challenging issues such as low anode activity and coke deposition. Therefore, development of active ceramic anode for SOFC has attracted great attention recently in particular, from preventing coke deposition. Mixed-conducting oxides with high reliability are gaining wide interest as alternative anode materials for this aim. Here we report surface modified as an active oxide anode for direct high carbon fuel type SOFCs.
Previously large power density and good coking tolerant was reported on both mixture, Ce(Mn,Fe)O2/La(Sr)Fe(Mn)O3 for dry propane, i.e. the maximum power of approximately 1 W cm-2 at 1073K, when dry propane and butane was used as a fuel. In this study, due to enhance catalytic performance and electron conductivity in oxide anode, we tested anodic properties of the oxide anode modified with the small amount of various additives. We evaluated the performance of surface modified on each oxide anode with various transition metal (Ni, Co, Fe), prepared by infiltration method. Ni infiltrated Ce(Mn,Fe)O2 shows the fairly good maximum power density of 500 mWcm-2 at 1073K in hydrogen atmosphere, 130 mWcm-2 in propane atmosphere. Furthermore, it will be therefore concluded that novel method for robust ceramic electrode with nano complex could be used as an active oxide electrode in solid oxide fuel cells and solid oxide electrolysis with excellent redox and coking tolerance under high carbon contents.

Keywords: oxide anode, ceria, Solid oxide fuel cells

100 - ABS 110

HYDROTHERMALLY SYNTHESIZED TUNGSTEN TRIOXIDE NANOROD ARRAY AND ZINC OXIDE NANOSHEET ARRAY COMPOSITION STRUCTURES FOR ENHANCED PHOTOCATALYTIC PROPERTIES

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Nanostructured oxide semiconductor photocatalysts have received great interest because of its ability to convert solar energy into electrical energy and its use in removal of hazardous organic pollutants from the wastewater. Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor, which is only excited under ultraviolet (UV) light illumination cause to inhibit its practical application. The modification or combination of ZnO with other narrow band gap oxide semiconductor can harvest more solar light, promote interfacial electron transfer, reduce photo-generated electron-hole pair recombination, and improve the photocatalytic performance. Tungsten trioxide (WO3) with narrow band gap energy of 2.8 eV possesses excellent optoelectrical properties. Hybridizing of ZnO with WO3 can form a more negative conduction band level that is an effective way to enhance the photo-induced charge separation efficiency and visible light-driven photocatalytic activity. In this study, hydrothermally growth WO3 nanorod (WNR) array onto the indium tin oxide (ITO) coated glass and ZnO nanosheet (ZNS) array on the WNR to produce visible-light-derived nanocomposite photocatalysts. X-ray diffraction (XRD) analysis confirmed the as-synthesized WO3/ZnO nanocomposites comprised of monoclinic and hexagonal structure of WO3 and ZnO. Brunauer–Emmett–Teller (BET) study revealed that the WO3/ZnO nanocomposite had higher surface area than those of the WNR and ZNS arrays. The band gap energies of WNR and ZNS arrays, determined from Tauc plots, were 2.5 eV and 3.2 eV, respectively. The peak wavelengths of the band edge emission evaluated from photoluminescence spectra were consistent with absorption edges determined from optical absorption spectra. In addition, the degradation of methylene blue (MB) and methyl orange (MO) in as-synthesized WNR array, ZNS array, and WO3/ZnO nanocomposites is carried out and the absorbance changes of MB and MO over time are reported.

Keywords: WO3/ZnO nanocomposite, Hydrothermal method, Photocatalysis

101 - ABS 732

OPTIMIZATION OF M-DOPED STRONTIUM FERRITE SYMMETRIC ELECTRODE AND CERAMIC ELECTROLYTES FOR SYMMETRICAL SOLID OXIDE FUEL CELLS

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Compared to traditional solid oxide fuel cells (SOFCs), symmetrical solid oxide fuel cells (SSOFCs) have attracted great attention because of several advantages as follows; the mechanical and chemical compatibility between the electrolyte and electrodes by reducing the number of different cell components and interfaces and much easier production of SSOFC because of assembly of the electrolyte and electrodes from just one thermal process, reducing fabrication time and costs. Among the redox stable electrode candidates, high valence metal ion-doped strontium ferrite, M-doped SFO (M= Ti4+, Si4+, Zr4+, Mo6+ and W6+), was reported to possess high redox stability in a wide range of temperatures and oxygen partial pressures. In particular, Ti-doped SFO is one of the most promising materials due to its relatively low polarization resistance and chemical compatibility with different electrolytes (i.e., GDC, LSGM). In this regard, we used composite electrodes of Ti-doped SFO and different electrolytes (i.e., YSZ, GDC, LSGM, and LSGMZ) for both cathode and anode in SSOFCs in order to improve electrochemical performances. First, Sr0.8Fe1-xTixO3-δ(x=0.2) was prepared by solid state reaction. The doping of Ti in SFO was confirmed by various tools such as powder X-ray diffraction, energy dispersive spectroscopy, x-ray absorption spectroscopy and so on. The composite materials of SFTO and different electrolytes were prepared by mechanical mixing using a ball miller and subsequent heat treatment. Among electrolytes used, it was confirmed that YSZ is not suitable for use as an electrode material because of an occurrence of secondary phases, evidenced by PXRD. Among the others, the composite composed of SFTO and LSGMZ exhibited the highest efficiency operating as both cathode and anode with polarization resistance values of 0.3 ohm/cm^2 in cell condition test at 750 °C. The SSFC consisting of LSGMZ electrolyte and symmetric SFTO/LSGMZ composite electrodes showed a maximum power density of 500 mW/cm^2 at 750 °C. In this presentation, we will discuss our recent efforts in using the composite electrodes in SSOFC, which include a synthesis procedure of materials, structural redox stability, and electrochemical performance.

Keywords: Symmetric SOFC,M-doped SFO, ceramic electroytes

102 - ABS 23

SYNTHESIS OF CERAMIC MATERIALS BASED ON Ca-Co-O SYSTEM BY CITRIC ACID METHOD

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Cobaltite ceramics represent an important category of thermoelectric materials. A huge point of interest, especially in high-temperature and energetic applications is dedicated them due to their feasible thermoelectric performance (i.e. maximum power factor, low thermal conductivity and electrical resistivity). The synthesis of Ca3Co4O9 phase and its processing is discussed within this work. As a major way of synthesis, the citric acid wet method was chosen. In order to prepare the single-phase product, the different reaction conditions were applied. The influence of raw materials input, a various molar ratio of EDTA to citric acid, the different stoichiometry of the starting materials or the effect of the firing conditions was observed. The simultaneous differential thermal and thermogravimetric analysis (TG-DTA), X-Ray diffraction analysis and scanning electron microscopy were performed to characterize the synthesized powders. Prepared samples were ball-milled with organic binder additive and un-axially pressed to pellets. The sintering conditions were studied by heating microscopy. Final products were examined by means of phase composition, microstructure and electrical properties.

Keywords: Cobaltites,Thermoelectric materials,Citric acid method

103 - ABS 733

FABRICATION OF TRANSPARENT CALCIUM LANTHANUM SULFIDE CERAMICS BY OPTIMIZING THE HEATING RATE IN SPARK PLASMA SINTERING

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The refractory ternary sulfide, calcium lanthanum sulfide(CaLa2S4, CLS) has the long infrared(IR) transmittance wavelength, excellent mechanical strength and high resistance to rain erosion. Therefore it is considered to be a promising candidate to replace traditional sulfides as IR optical ceramics for applications in harsh environments. Spark plasma sintering(SPS) is a rapid sintering technology that has enabled densification under a relatively lower sintering temperature and fine microstructures. In this study, the effect of heating rate on the transparency of CLS ceramics in SPS process was investigated systematically. Densification and microstructural developments during the process were also discussed.

Keywords: calcium lanthanum sulfide, transparent ceramics, spark plasma sintering

104 - ABS 916

STRUCTURE AND ELECTRICAL PROPERTIES OF YTTRIUM OXIDE FIRED BY SPARK PLASMA SINTERING OR SPRAYED BY PLASMA TORCH

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Yttrium oxide Y_2O_3 ceramics was fired by spark plasma sintering (SPS) using a nanometric powder. Influence of the SPS process and subsequent annealing on microstructure, phase composition and dielectric properties was studied. The color of this material was proven as insensitive to dramatically reducing atmosphere in the SPS apparatus (necessary for the process because of carbon pistons and die used for powder compaction). After subsequent annealing in air the density of the product increased due to defect healing. Dielectric properties were studied in a broad range of frequencies.

Yttrium oxide was also sprayed by plasma torch using a coarse thermal spray powder, which must be in size range of tens of micrometers because of penetrating condition into the plasma stream. Thick coatings on steel substrates were produced. The color of Y_2O_3 ceramics was proven as insensitive to dramatically reducing conditions in the spray apparatus (that are caused by hydrogen used as a component of the plasma forming medium). Dielectric properties were studied in a broad range of frequencies. Moreover the favorable geometry of thick coatings enabled us to measure dielectric strength of the Y_2O_3 ceramics.

The microstructure aspects as well as crystallite size, micro strain and presence / absence of textured crystallization were analyzed and discussed in connection with electrical properties of yttrium oxide fabricated by both techniques.

Keywords: yttrium oxide, plasma spay, spark plasma sintering

105 - ABS 915

THE EFFECTS OF RARE EARTH DOPING ON PERSISTENT PHOSPHORESCENCE PROPERTIES OF ZINC BOROSILICATE GLASSES

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Ceramic based phosphors, like CaAl2O4: Eu2+, Nd3+ (blue) and SrAl2O4: Eu2+, Dy3+ (green), are known as popular for long lasting phosphorescence. They can emit light even for several hours after the removal of the light source. On the other hand, glass phosphors are very versatile materials and have various application area due to their high transparency, homogeneity and can be easily fabricated to various forms. These phosphors attract considerable interest due to their promising application for energy saving and enhancement of the conversion efficiencies of solar cells. However, their low intensity and relatively short afterglow time limit their industrial adaptation. In the present study, transparent glasses which desired to gain high brightness and long lasting phosphorescence doped with rare earths and irradiated by UV-254 lamp. Zinc borosilicate glasses with persistent phosphorescence properties are synthesized and doped/co-doped with rare-earths and characterized by using XRD, DTA and Spectrophotometer. The effects of cooling rate, heat treatment temperature/time, excess boric acid and the rare-earth co-doping (Tm, Gd and Ce) on luminescence of zinc borosilicate glasses have been investigated and enhancement on the luminescent intensity was observed with the addition of Tm as co-dopant. Also, a change in phosphorescence properties was observed by adding sodium oxide instead of zinc oxide to the host glass in order to gain phosphorescence property to the sodium borate glasses.

Keywords: Transparent glass, Phosphorescence, Rare earth co-doping

106 - ABS 914

ELABORATION AND CHARACTERIZATION OF CERAMICS MATERIALS FOR ELECTRONIC APPLICATIONS

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With the size reduction of microelectronic devices, high-dielectric-constant materials have become increasingly important. Recently, much attention has been paid to CaCu3Ti4O12 (CCTO), these ceramics are also attractive for capacitor applications and certainly for microelectronics. CCTO powders were prepared by the solid state traditional method. At first, stoichiometric quantities of CaCO3, TiO2 and Cu2O were mixed in alcohol for 6h, and the mixture was calcined at 1100 C for 6h, then the calcined powder was pressed into pellet and sintered at various sintering temperatures. The crystalline structure of the calcined powder and of the sintered samples was characterized by X-ray diffraction (XRD), the microstructures of ceramics were observed by scanning electron microscopy (SEM). The relative bulk densities of the sintered pellets measured by the Archimedes method. The dielectric constant and loss were also studied in the medium-frequency range 20 Hz to 1 MHz.

Keywords: Ceramics, ccto, Dielectric properties

107 - ABS 651

LTCC DEVELOPMENT OF LOW-K AND MID-K CO-FIRED MATERIALS AND SILVER DIFFUSIVE BEHAVIOR

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The low-K and mid-K co-fired microwave dielectric materials for the development of low temperature co-fired ceramics (LTCC) were investigated. The mid-K material is Ba5Nb4O15 ceramic added with <10% glass (BN-40). The low-K materials include BaWO4 ceramic added with <10% glass (BW-10), CaMgSi2O6 glass-ceramics (Diop-7), and CaO-SrO-Al2O3-B2O3-SiO2 glass added with Al2O3 ceramic-filler (CSABS-7). ER-40 and ER-10 contain less than 3% silicate oxide addition, and Diop-7 and CSABS-7 contain high concentrations of silicate oxide up to above 50%. In order to develop the heterogeneous co-firing of low-K and mid-K materials, four materials were prepared by tape casting and then low/mid-K materials co-fired at 900oC for 30 mins with Ag electrode.

The BN-40 co-fired with both Diop-7 and CSABS-7 shows high Si diffusion in the heterogeneous boundary. Diop-7 and CSABS-7 co-fired with silver inner-electrode also exhibit high silver diffusion in the matrix. It was suggested that the liquid phase sintering easily induces interaction and silver diffusion due to the high silicate concentration. Moreover, the BN-40 co-fired with BW-10 exhibits clearly heterogeneous boundary and no Ag diffusion due to a few silicate existence in theBN-40 and BW-10. BN-40 and BW-10 can be considered as candidates for low-K and mid-K co-fired materials for LTCC development.

Furthermore, the silver diffusion of Diop-7 and CSABS-7 was analyzed. In the CSABS-7 system, the higher sintering temperature and the longer soaking time increase silver diffusion distance to comply with the Fick's second law. In the glass-ceramics of Diop-7, silver obviously diffused into matrix while nucleation took place. In this study, the DSC results show an exothermic peak in the region of 820-840 oC, corresponding the nucleation temperature of CaO-MgO-SiO2 glass-ceramics. XRD results show the t-phase ZrO2 nucleation from 820oC to 840oC. The XRD Rietveld results show that the crystalline contents of diopside are 7.5% for nucleating temperature at 825oC and 51% for crystal growth at 900oC. EPMA-mapping result for specimens co-fired with Ag electrode during nucleating temperature exhibits obvious silver diffusion in the matrix. The TEM-EDS results show higher silver concentration aggregation around grain boundary of diopside phase, which could be attributed to localized exothermic phenomenon during embryo evolution at the nucleating temperature.

Keywords: LTCC, glass-ceramic

108 - ABS 903

RHEOLOGY STUDY OF SLURRY MADE WITH $Ca(Zr_xTi_{1-x})O_3$

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The solid-state domain of CaTiO3/CaZrO3 perovskites is controversial. It seems that the results of the limits of this domain change with the method of synthesis (Ref. 1). In order to resolve this problem, we chose to optimize the solid-state method, especially the dispersion of the raw powders (CaCO3, TiO2 and ZrO2) in the slurry. This work consist in a rheological study of the blending of the raw powders with the aim of produce several composition of the Ca(ZrxTi1-x)O3 system. The selected zirconium's proportions are x=1 ;0,8 ;0,7 ;0,5 ;0,3 ;0,2 and 0 to determine the better conditions of dispersion for an attrition blending and milling.
The rheological behavior of the aqueous slurries, with mass concentration of 50% (between 20 and 24% by volume according to the different compositions), was analyzed with a rotating cylinder rheometer. The range of shear rate was from 1 to 1000 s-1. The influence of the pH was examine, but his effect did not liquefy enough the slurries. However, the addition of dispersing agent in different amounts allow modifying the slurries' rheological behavior (Fig. 1). The study shows that we pass from a shear thinning with high viscosities values at low shear rate to a shear thickening, nearly Newtonian, with low viscosities values for every shear rate. We determined for every composition the optimum amount of dispersing agent to add.
The X-Ray diffraction analysis of the calcined powers show that we obtain single phased powders of some solids solutions (Fig. 2), which are hard to obtain when the blending parameters are not enhanced. (Ref 2,3).

Ref:
(1) : Solid-State Phase Relationships in the Calcia-Titania-Zirconia System at 1200°C, Swenson et al., Journal of the American Ceramic Society 1998
(2) : High-energy density dielectrics and capacitors for elevated temperatures: Ca (Zr, Ti) O3; Lee Haijoon et al., Journal of the American Ceramic Society 2013
(3) : Solubility limits and microwave dielectric properties of Ca(ZrxTi1-x)O3 solid solution, Parida et al.

Keywords: Ceramic Capacitor,Rheology,CZT System

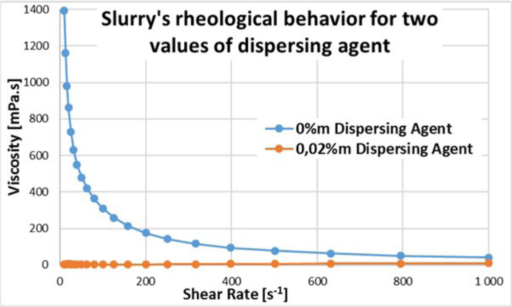

Figure 1: Evolution of the rheological behavior of $Ca(Zr_{0,5}Ti_{0,5})O_3$ raw material's slurry depending on the shear rate for two different values of dispersing agent

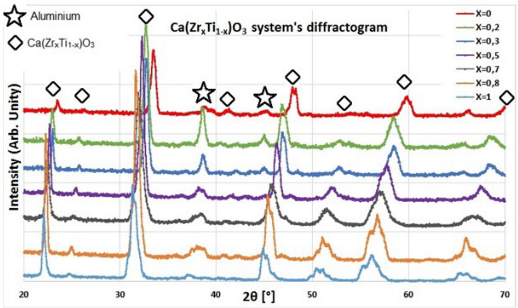

Figure 2: X-Ray diffractogram of the different compositions of the $Ca(Zr_xTi_{1-x})O_3$ system

109 - ABS 925

ADDITIVE STABILIZATION OF MAGHMITE FOR USE AS A PHOTOCATALYST

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Maghmite (γ-Fe_2O_3) is a less common polymorph of hematite, the famous iron oxide. Although these two share the same chemical formula, its properties can differ significantly. Maghmite has a cubic structure and it is a metastable phase present at higher temperatures. It has good magnetic properties, can act as photocatalyst and is biocompatible. The difficulty is to obtain stable γ-Fe_2O_3 at room temperature as α-Fe_2O_3 (hematite) is the thermodynamically stable phase at this temperature. However, some phenomena are capable of stabilizing more of the γ phase, like interface segregation. When additives are added to a system, among other paths, they can segregate at the interfaces (i.e. free surface or grain boundary) and modify the energy of the interface then changing the thermodynamically stable phases. Powders were prepared by the polymeric precursors method with different amounts of dopant (0, 1, 3, 5 and 10 mol%). The use of volatile dopants such as chloride (Cl) and fluoride (F) increased the mass fraction of maghmite, changed the microstructure and final concentrations of the dopant were non-detectable for some samples and for others remained below 1 mol%. Magnetic force was greatly improved due to the high contents of maghmite and it is proportional to the stabilization of maghmite nanoparticles and increase in the total specific surface area. Doped Fe_2O_3 is currently in test for photocatalyst applications.

Keywords: iron oxide, maghmite, photocatalyst

110 - ABS 909

GEL COMBUSTION SYNTHESIS AND LUMINESCENT PROPERTIES OF RARE-EARTH CO-DOPED $CaTiO_3$ RED PHOSPHORS

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Rare-earth doped calcium titanate (CaTiO3) phosphors which are novel luminescent materials with advanced physical-chemical properties, have attracted significant attention owing to their promising photoluminescent properties and potential applications in white light-emitting diodes (LEDs) due to very close to the chromaticity coordinates of the ideal red. However, these materials still cannot meet desirable luminescence intensity and afterglow time properties for advanced flat-panel displays. In the present study, to improve red luminescence and the afterglow intensity of Pr3+ activated calcium titanate, rare-earth elements and transition metals are used as co-dopant. Citrate-nitrate gel combustion method adopted to obtain homogeneous distribution of doping /co-doping elements and the results were also compared with the conventional powder preparation techniques. The samples were characterized by using, SEM, XRD, and Spectrophotometer. The effects of phase transition of calcium titanate on the phosphorescence properties were also investigated by changing of sintering temperature and condition. A significant enhancement on the luminescent intensity was observed with the addition of the Lu3+, La3+, Eu3+, Y3+ as co-doping.

Keywords: red phosphors, co-doping, optical ceramics

111 - ABS 563

HYDROGEN EFFECT ON THE OPTICAL AND MECHANICAL PROPERTIES OF SIN THIN FILMS

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Objective Silicon nitride is an important material in several applications from engine components to cutting tools [1]. Its properties, like high thermal stability, chemical inertness, hardness, and good dielectric behavior, make it more attractive and most commonly used material [2]. Furthermore its transpareny over a wide spectral range from near ultraviolet to infrared region makes it suitable for several optical application. [3]

It is also known that the use of other ions, such as hydrogen during the process can also produce unique materials with special properties. [4] The aim of this study is to investigate the effect of hydrogen content on the optical and mechanical properties of silicon nitride thin films.

Materials/Method Silicon nitride thin films were deposited on silicon wafers and glass substrate by Radio Frequency Sputtering. Various amounts of hydrogen was added during the sputtering process. Structure of the sputtered films were investigated and layer thicknesses were determined by transmission electronmicroscopy. The optical properties of thin films were examined by spectroscopic ellipsometry and UV-VIS spectroscopy. X-ray Photoelectron Spectroscopy and Fourier Transform Infrared spectroscopy were used to identify the composition and chemical bonding configuration of sputtered films. Mechanical properties were studied by tribometer.

Results Transmission electronmicroscopy measurements have proved that the sputtered layers are amorphous furthermore layer thicknesses were around 150 nm. Results of ellipsometry showed that increasing the hydrogen content during the sputtering process results lower refractive index of the sputtered film. According to the results of tribology adding hydrogen improves the mechanical resistance of sputtered films.

Conclusion Hydrogenated silicon nitride thin films were sputtered on Si-wafers and glass. Ellipsometry and tribology measurements revealed that the optical and mechanical properties of silicon nitride can be improved by adding hydrogen.

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Keywords: Hydrogenated silicon nitride,RF sputtering deposition,Ellipsometry

112 - ABS 554

MICROSTRUCTURAL AND OPTICAL PROPERTIES OF THE ZnS CERAMICS OBTAINED BY SPARK PLASMA SINTERING OF HYDROTHERMALLY SYNTHESIZED POWDERS

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Zinc Sulfide (ZnS) is a kind of infrared optical materials with excellent physical and chemical properties, and it has high transparency in the range of 3~12 μm. High purity ZnS can be used as infrared window and missile dome in defense applications. ZnS has a cubic sphalerite structure at low temperature, and it changes to hexagonal wurtzite structure at 1020 ^oC. The existence of hexagonal phase can cause birefringence that greatly decrease the optical transparency of ZnS material. To solve this problem it is effective to inhibit grain growth in these two phase mixture systems to improve their optical properties. In this study, ZnS nanopowder was hydrothermally synthesized. Their microstructural properties on annealing under vacuum condition were characterized by scanning electron microscope and Fourier Transform Infrared (FT-IR) spectra. Using synthesized powders ZnS ceramics were consolidated by spark plasma sintering under various conditions and their optical properties were also discussed.

Keywords: ZnS nanopowder,Hydrothermal synthesis,Spark plasma sintering

113 - ABS 546

COLOR-TUNABLE Dy^{3+}/Tb^{3+} CO-DOPED LILA$(MoO_4)_2:Sm^{3+}$ PHOSPHORS FOR SINGLE-PHASED WHITE-LIGHT-EMITTING LUMINESCENCE

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LiLa(MoO4)2:Sm3+ phosphors were prepared via the conventional solid state route. It processed a comparably high intensity concentration at Sm3+= 9% for LiLa(MoO4)2 host excited with a source 276 nm. The concentration quenching mechanism that was owing to the exchange interaction was also discussed. At different calcine temperatures, the host material shows two different crystal structures which are orthorhombic (<650°C) and tetragonal (<650°C) that emitted red-orange light and pink-purple light, respectively. The decrease of the fluorescence intensity caused by the charge compensation factor could be eliminated by doping either Dy3+ or Tb3+ into the LiLa(MoO4)2:Sm3+ phosphors. The emission color of LiLa(MoO4)2:Sm3+/Dy3+ and LiLa(MoO4)2:Sm3+/Tb3+ could be tuned to white by varying co-doping concentrations of Sm3+/Dy3+ and Sm3+/Tb3+ ions and they were proposed as a very promising single-phased white-emitting phosphor for white LEDs devices.

Keywords: single-phased white-light-emit,LiLa(MoO4)2,color-tunable photoluminescenc

114 - ABS 469

PREPARATION AND CHARACTERIZATION OF METAL TRI-DOPED Y_2O_3 FOR MAGNETO-OPTICAL APPLICATION

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This research are focuses on a citrate preparation method of Bi0.1Y1.9O3, Er0.1Y1.9O3, Yb0.1Y1.9O3 and tri doped Bi0.1Er0.1Yb0.1Y1.7O3 transparent ceramic, for application in magneto-optical devices and their physicochemical characterization. The preparation method is based on a sol–gel technique using metal nitride, by use citrate acid and glycol as fuel. This modified procedure yielded fine-crystalline powders with a narrow grain size distribution, which made it possible to obtain dense sinters with low total porosity and, subsequently, a fine-crystalline microstructure. On the basis of differential scanning calorimetry and thermal analysis measurements, the temperature of calcinations have been determined. Fourier Transform -Infrared spectra are very similar and shift in vibration bands was not observed. X-ray diffraction phase tests for the Y2O3 powders confirmed the homogeneous bixbyite structure. Vacuum sintering method was applied for preparation of polycrystalline single and tri-doped Y2O3 transparent ceramic with sub micron grain size. The effect of ions metals to influence both densification and grain growth of yttira, on microstructure development was studied by scannning electron microscopy. Chemical compounds of all sample was confirmed by Energy dispersive X ray Analysis. Relative density for all sinters was over 99.5 % and grain size was measurements. The structural analysis of the pure and doped Y2O3 samples, only the cubic crystal structure with the Ia-3 space group was found. All Raman spectra are characterized by the presence of a very strong band in the range 450–3500 cm - 1, depending on the type of ion doped. Optical linear transmittances in the visible –near infrared wavelength region for doped Y2O3 ceramic could reach as high as above 70%. Verdet constant was measurement in wide range 300-1100 nm with 5 nm step in room temperature. Verdet constant was achieve over 1000 deg/Tm in Bi0.1Er0.1Yb0.1Y1.7O3 sample in optical region. Figure of merit of Verdet constant for all samples were computed. What should be highlight, in contrast to garnet crystals the Verdet constant is independent of measurement point. Luminescence properties in VIS and IR region were measured. The CIE chromaticity coordinates of Bi0.1Y1.9O3, Er0.1Y1.9O3, Yb0.1Y1.9O3 and Bi0.1Er0.1Yb0.1Y1.7O3 were conducted. The prepared materials therefore appear suitable for a wide range of applications in electro-optics and magneto-optics. This investigation was financed by the National Science Centre, Poland, project number 2016/23/D/ST8/00014

Keywords: Y_2O_3,Transparent ceramics,Verdet constant

115 - ABS 888

FABRICATION AND CHARACTERIZATIONS OF HfO_2-BASED BILAYER ULTRATHIN FILM MEMRISTORS FOR ELECTRONIC SYNAPSE APPLICATIONS

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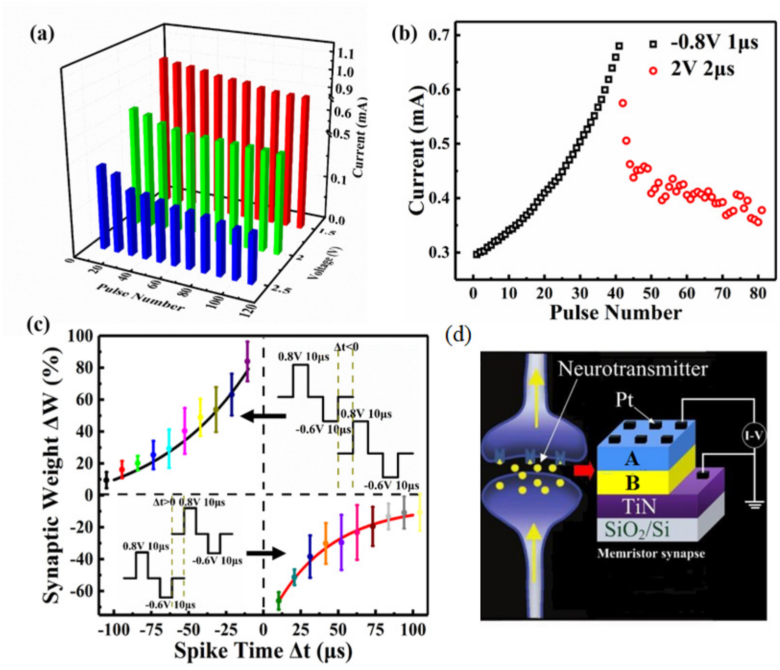
Synapse is the smallest unit of learning and memory of human brain, and the bionic simulation of synaptic learning is considered as an important route to realize artificial neural network. Ordinary electron devices use a number of transistors and capacitors to realize artificial synapse, causing high energy dissipation at high density and the limitation of software program running. The new memristor system is now known as the most close to the synaptic device because of its nonlinear transfer characteristics similar to the neural synapse. In this work, HfO2-based bilayer ultrathin film memristors, such as Pt/HfO2/HfOx/TiN, Pt/AlOx/HfOx/TiN, and Pt/HfOx/ZnOx/TiN were fabricated by atomic layer deposition. With the aid of X-ray photoelectron spectroscopy, the non-uniform distribution of oxygen vacancies in the HfO2-based bilayer ultrathin film has been confirmed. In the Pt/AlOx/HfOx/TiN device, the formation/rupture of nanoscale conductive filaments of oxygen vacancies probably occurs in the AlOx layer due to more oxygen vacancies in the oxygen-deficient HfOx layer than the AlOx layer. The thickness of filaments could be altered with the amplitude and width of the stimulating pulses. With the conductive filaments becoming narrow to a quantum wire, the quantum conductance has been observed during bipolar reset process of HfO2-based bilayer ultrathin film memristors. The synaptic plasticity and learning behaviors of bilayer memristive system were investigated deeply. Several essential synaptic functions are simultaneously achieved in such an ultrathin HfO2-based bilayer-structure device, such as nonlinear transmission characteristics, spike-timing-dependent plasticity, paired-pulse facilitation, long-term/short-term plasticity, and conditioned reflex. The low energy consumption per operation has been evaluated in about ten-picojoule range. A memristive switching mechanism of bilayer metal oxide synaptic device has been proposed to explain synaptic plasticity based on oxygen vacancies migration/diffusion model. The HfO2-based bilayer structures memristors may be promising electronic synapse devices for the emerging neuromorphic computation system.

Keywords: HfO2-based bilayer structure,Memristor,Atomic layer deposition



116 - ABS 431

THE PREPARATION AND OZONE GAS-SENSING PERFORMANCE OF Co_3O_4 NANOBRICKS

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Ozone (O3) is widely used, but it is harmful to human health. It is necessary to develop a device to monitor the concentration. However, the traditional metal oxide based sensors are insensitive to ozone. In this paper, uniform Co3O4 nanobricks were prepared by a hydrothermal corrosion method using CoSn(OH)6 as precursor. The phases and morphologies of the precursor CoSn(OH)6 and the Co3O4 nanobricks were examined by XRD, SEM and TEM. The Co3O4 nanobricks were face-center cubic structure Co3O4 (JCPDS No.71-0816). The average nanocrystal size of the Co3O4 nanobricks was 10.2 nm. From the SEM, the shape of Co3O4 nanoparicles were bricks and the size was about 100 nm, From the TEM and crystal size estimated by XRD, we deduced that the Co3O4 nanoparticles are composed of small nanocrystals.
The sensor based on the Co3O4 nanobricks showed gas sensing to ethanol, acetone and ozone. The resistances of the Co3O4 nanobricks sensors increased when ethane or acetone gas was introduced, and the responses showed the trend of “increasing-maximum- decreasing”. The optimal operating temperature of the Co3O4 sensor to ethanol and acetone are 200°C, and the maximum responses are 30, 24 to 100 ppm ethane and acetone, respectively. The resistance of the p-type Co3O4 sensor decreased when the ozone was introduced. The response showed the maximum of 65 to 100 ppm ozone at the optimal operating temperature of 80°C. The optimal temperature was very different between the reducing gas and ozone. It implied the response resulted from different gas-sensing mechanisms. The response value of the Co3O4 sensors increased with an increasing ozone concentration at their optimum operating temperatures, the responses of the sensor increased without saturation limits up to the maximum ozone content in air. The response and recovery time of the sensor were 25 s and 45 s, respectively. In addition, the sensor showed the repeatability and long-term stability to ozone in ten weeks. The Co3O4 nanobricks are a promising candidate gas-sensing material for fast, sensitive and selective detection of ozone.

Keywords: Co3O4 nanobricks,,ozone,gas-sensing

117 - ABS 428

NEW THERMAL-SENSITIVE PROPERTIES OF BiTiO$_3$ CERAMICS FOR HIGH TEMPERATURE NTC THERMISTORS

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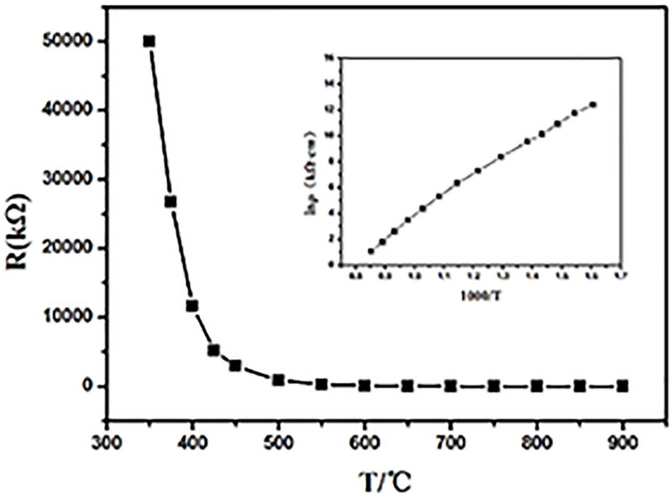
In our research it was firstly found that BiTiO3 ceramic showed negative temperature coefficients (NTC) . The BiTiO3 were successfully prepared by the Pechini method . The BiTiO3 ceramic exhibited a good linear relationship between logarithm of electrical resistivity and reciprocal of absolute temperature (1000/T) in 100-800 Celsius degree. The obtained ρ300, ρ 600 and B300/600 constants of the BiTiO3 NTC thermistor are about 2.7×106, 3.2×104 Ohm cm, 7.4×103 K, respectively. The electrical conductivity in these compounds is due to the electron jumps between Ti3+ and Ti4+, and oxygen-ion conductivity.



Stoichiometric amounts of Bi2O3 (Sigma–Aldrich, USA, 99.99%), TiO2 (Sigma–Aldrich, USA, 99%) were well mixed, ground, and calcined at 650 Celsius degree for 2 h to yield BiTiO3. Then, the powder was milled again for 6 h. The calcined powders were then ground and pressed into disks of 8 mm in diameter and 2.5 mm in thickness at die pressure of 10 MPa and was sintered at 1100 Celsius degree for 2 h.

The relationship between electrical resistivity and absolute temperature for BiTiO3 samples is shown in picture. The resistivity decreases exponentially with increasing temperature. The relationship between log ρ and the reciprocal of absolute temperature (1/T) for the BiTiO3 samples is shown in the inset of picture A linear relation between log ρ and (1/T) two parameters indicates that the samples possess the NTC thermistor characteristics, as is described by the following Arrhenius equation: ρ = ρo exp(Ea / kT), where ρo is the resistivity of the material at infinite temperature, T is the absolute temperature, Ea is the activation energy for electrical conduction and can be calculated from the slopes of the ln ρ versus 1/T plots, and k is the Boltzmann constant. In addition, the thermistor constant B, which indicates a sensitivity to temperature excursions and is given by B=Ea / K. Bi-based materials exhibit high known oxygen-ion conductivity. The high ionic conductivity originates from oxygen vacancies generated due to Bi-deficiency, as well as high anion mobility as a result of highly polarisable. Bi3+ with its 6s 2 lone pair electrons and weak Bi-O bonds, which provide pathways with low diffusion barriers.

BiTiO3 NTC quaternary materials have been prepared successfully by conventional solid state reaction. The resistivity decreases exponentially with increasing temperature. The electrical conduction of the BiTiO3 perovskite ceramic can be well described using the ion migration mechanism and oxygen-ion conductivity.

Keywords: NTC thermistors, Perovskite ceramics, Electrical properties

118 - ABS 220

HYDROTHERMAL SYNTHESIS OF NEW BKBO BASED DOUBLE PEROVSKITE SUPERCONDUCTOR

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Introduction The hydrothermal synthesis is useful synthetic route for new bismuth based oxide with a variety of structures like pyrochlore and perovskite type structures. Some of these exhibit unique properties such as photocatalysis and superconductivity. In our research a new bismuth based superconductor (Ba0.59K0.41)4Bi4O12) with double perovskite-type structure was prepared by hydrothermal reaction using KBiO3. The crystal structure of these compounds were refined by single crystal X-ray diffraction. We will described preparation, crystal structure and superconducting properties.

Experimental Crystalline samples were synthesized under hydrothermal conditions in aqueous solutions with a Teflon-lined autoclave using the starting materials, KBiO3, Ba(OH)2•8H2O, and KOH in a 1: 1: 240 molar ratio, respectively, put 12 mL distilled water and heated 240 °C for 2 days. Crystal structure was determined by X-ray powder diffraction using monochromated CuKα radiation and refined from single crystal X-ray diffraction data. EPMA determined the chemical composition of the crystal sample. Crystal structure was visualized using VESTA. The temperature dependence of the DC magnetic susceptibility was measured in zero-field-cooling and field cooling with a vibrating sample magnetometer (PPMS, Quantum Design). The temperature dependent electrical resistivity of the pressed pellet was measured using a standard four-probe method (PPMS, Quantum Design).

Result and Discussion The XRD pattern of highly crystalline powder hydrothermally synthesized at 240 °C was indexed as double perovskite like phase with the cubic cell of space group Im-3m (No.229). The crystal structure was refined based on single crystal X-ray diffraction of large cubic crystal. The R1 and wR2 value of the refinement were 0.0078 and 0.0136 (all data) respectively. The chemical composition of the material was determined by electron probe micro analysis which was well consistent with the refined data. The lattice parameter derived from the single crystal refinement was a = 8.5207 (2) Å. The fabricated compound exhibited the largest shielding volume fraction compared to previously reported Bi based superconducting double perovskites with a maximum T_c^mag of ~30 K. Its electrical resistivity dropped at ~25 K and zero resistivity was visualized below 7 K. Thermal behavior analysis revealed that the double perovskite structure was transformed to single perovskite one with no diamagnetic signal at 600 °C. The calculated band structure confirmed the metallic characteristics and the O 2p and Bi 6s, 6p orbital electrons primarily contributed to the DOS at Fermi level for this new double perovskite superconductor.

Keywords: Hydrothermal method,Double perovskite structure,Superconductivity

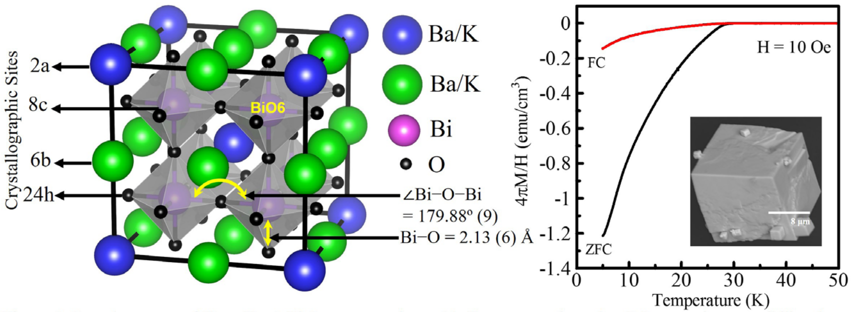

Figure 1. Crystal structure of $(Ba_{0.59}K_{0.41})_4Bi_4O_{12}$ superconductor (a); Temperature dependent DC magnetic susceptibility, the insert shows single crystal (b)

119 - ABS 201

NANOCASTING SYNTHESIS OF MESOPOROUS SnO_2 FOR HUMIDITY SENSOR APPLICATION

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This work presents the fabrication of humidity sensor based on SnO2 sensing material derived by the nanocasting process using hydrothermally obtained KIT-5 as a hard template.

In a typical wet impregnation process, the infiltration of Sn precursor into mesoporous silica KIT-5, and later evaporation of the solvent were conducted to fill pores to 15 % of the template pore volume. The calcination and removal of the template were performed to obtain the desired mesoporous SnO2. The obtained powder (P) was mixed with a 10 % ethyl-cellulose in α- terpineol solution (S) and acetic acid (A) in the weight ratio P:S:A=7:69.7:23.3 to form a homogeneous paste which was further deposited by doctor blade technique onto alumina substrate with screen printed Pt/Ag electrodes. The film was subjected to a specific drying regime and finally calcined at 550 °C for 5 h.

The obtained SnO2 nanoparticles as well KIT-5 template were characterized using X-ray diffraction (XRD) spectroscopy, Brunauer–Emmett–Teller (BET) analysis and Transmission Electron Microscopy (TEM). Cross section and surface morphology of SnO2 film were characterized by Field Emission Scanning Electron Microscopy (FESEM). The humidity sensing properties of the mesoporous SnO2 sensor were investigated in a JEIO TECH TH-KE-025 temperature and humidity climatic chamber in the range 30–90 % RH. Complex impedance spectra of the as-fabricated sensor were analyzed at room temperature and 50 °C with a HIOKI 3532-50 LCR HiTESTER in a frequency range 42 Hz - 1 MHz.

Nitrogen adsorption isotherms of KIT-5 showed high specific surface area of 610 m2g-1 and average pore diameter of 5.2 nm while those values for SnO2 sample were 33 m2g-1 and 19.9 nm respectively. Even though that mesoporous ordering of nanocasted negative replica was observed by TEM, the presence of agglomerates in SnO2, as well as the relatively low specific surface area of 33 m2g-1, confirm its partial degradation. Diffraction patterns from TEM display well-defined rings typical for cassiterite SnO2. The impedance measured at 42 Hz, at room temperature, and in the range 40-90% RH reduced 509 times, while at 50 °C it reduced 48 times. The sensor exhibited quick response (5 s) and recovery time (16 s) when it exposed to humidity change from 37% RH to 90% RH, and relatively low hysteresis of 3.2% observed at 40% RH and at room temperature showing its promising capacity as a humidity sensor.

Keywords: nanocasting, tin oxide, humidity sensors

120 - ABS 175

FABRICATION OF TRANSPARENT AND NANOSTRUCTURED DOPED AND UNDOPED $NaGdF_4$ GLASS-CERAMIC COATINGS FOR OPTOELECTRONIC DEVICE APPLICATIONS

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Crack-free, transparent and homogeneous undoped and doped Nd3+-90SiO2-10NaGdF4 glass-ceramic (GC) coatings have been prepared by sol-gel process for using in optical applications. The glass-ceramic (GC) films have been prepared by dip coating and heat treated at temperatures between 550°C and 650°C at different time intervals. The structural, thermal and optical properties have been evaluated and related to understanding the crystallization mechanism. By controlling the parameters of sol-gel process and deposition, such as molar ratio of precursors, water content, viscosity of the sol, the withdrawal rate, etc... the morphology and structural properties of the GC films can be designed.

The characterization has been performed by spectral ellipsometry to determine the thickness and refractive index of prepared coatings, by GI-XRD and HRTEM to document precipitation of the NaGdF4 nano-crystals and the content of crystalline phases in the SiO2 matrix, revealing the size of crystals in the nanometer scale. The emission and excitation spectra together with the luminescence lifetimes of the films have been evaluated as a function of thermal treatment and Nd3+ content. The luminescence intensity from the 4F 3/2 to 4I 11/2 laser transition was also explored. The present work presents a possible way of manipulation of structural, thermal and optical behavior of nanocrystals.

Keywords: Transparent coatings,Dip coating,NaGdF4 glass-ceramic

121 - ABS 967

SELF-ASSEMBLY OF POLYMER - CERAMIC NANOPARTICLES CLUSTERS INTO THIN FILMS OBTAINED BY SCREEN-PRINTING METHOD

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Printed electronics is an all-encompassing term for the printing method used to create electronic devices by printing on a variety of substrates. The development of next-generation electronic devices is closely linked to cross-coupling between different functional properties. Currently, multifunctional materials research is based on designing of meta-nanostructures or laminated nanocomposites for a useful combination of properties and applications. Particularly, modern technologies of printed electronics for MLCC, SOFC, DSSC require developing of appropriate structures in the form of thin layers with a smooth interface between functional layers. In this regard, we propose to solve this problem by developing a new scientific and methodical approach to the formation of the composition, structure, and properties of viscous dispersions based on nanopowders and polymers. It is related to controlling the structuring processes of suspensions under the influence of directed flow due to the change in the shape of the polymer molecule itself by plasticization. Designing the size and structure of clusters allow controlling the suspension structuration under directed flow and the further inheritance of this structure by the screen-printing films. Thus, the thin (0.7 – 0.8 μm) smooth (Ra = 20 – 25 nm) films of nanocrystalline BaTiO3 were obtained by the screen-printing method for MLCC production.

Keywords: self-assembly, nanoparcticles, thin films

122 - ABS 25

THE JUMP-LIKE PTCR EFFECT IN METAL-BaTiO$_3$ COMPOSITE MAGNETIC PTC THERMISTORS

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A composite composed of a highly conducting phase and a high-resistivity BaTiO3 phase was prepared. The high-resistivity BaTiO3 was realized using a high-temperature treatment, while metal powder was used as the conducting phase. The composite was prepared from a mixture of the constitutive phases: a highly conducting metal powder and high-resistivity BaTiO3 grains. The composition, the compacting pressure and the sintering temperature (under 1000oC) were optimized in order to obtain a low-resistivity (less than 1 ohmcm) metal-BaTiO3 composite with a remarkable, jump-like, anomaly (more than 10^3) in the electrical resistivity at the Curie temperature of BaTiO3. It was postulated that the PTCR anomaly was obtained exclusively as a result of the disconnection of the conducting metal network due to the volume changes associated with the phase transformation between the tetragonal and cubic BaTiO3 at the Curie temperature. Samples with PTCR effect showed also magnetic properties.
Microstructural analyses, scanning electron microscopy, dilatometry, magnetic and electrical measurements were used to characterize the materials that showed the PTCR (positive temperature coefficient of the electrical resistivity) effect and behaved as magnets.

Keywords: barium titanate, PTC thermistors, magnets

POSTER SESSION 2

1- ABS 843

FACILE SYNTHESIS OF YOLK-SHELL Fe_3O_4@SiO_2 NANO-SPHERES AND THEIR ADSORPTION PROPERTY FOR THE PLASMID DNA

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Fe3O4@SiO2 core/shell structured nanoparticles are promising materials in bio-field such as drug delivery system and nucleic acid purification based on superparamagnetic properties of Fe3O4 core and bonding capacity with other molecules of hydroxyl groups of silica shell. In this core/shell structure, the bonding capacity of the silica coating layer is increased by enhancing surface area, and it knows as well that the method for improving the surface area is to form a hollow or mesoporous structure. To fabricate inorganic hollow materials, the soft-templating method has been used generally, but the degeneration of a primary particle could be occurred in the template removal process due to thermal processing or use of strong acid or base.

In this study, therefore, Cetyl Trimethyl Ammonium Bromide (CTAB) which is a water-washable hydrophilic surfactant was used as a template, and synthesis of magnetic nanoparticle that has hollow interlayer and the mesoporous silica coating layer was performed. Additionally, the separate purification of Plasmid DNA was carried out with the manufactured particles.

As a result of the addition of CTAB, the surfactant layer was formed due to electrostatic attraction with Fe3O4 nanoparticle and CTAB. And it was confirmed that the morphology of the silica coating layer formed over the CTAB layer varies as the concentration of the surfactant.

Consequently, as the surface area of the silica layer increases, the adsorption site of plasmid DNA was advanced, so the purification concentration of plasmid DNA was considerably increased.

Keywords: yolk-shell structure, plasmid DNA, nano-sphere

2- ABS 594

FLAME SPRAY SYNTHESIS FOR THE PRODUCTION OF HIGHLY ACTIVE NANOCATALYST FOR OXYGEN EVOLUTION REACTION

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Flame Spray Synthesis (FSS) is a powerful route for the preparation of nanopowders with high specific surface area, high homogeneity and high crystallinity. Many setup parameters together with the chemistry of the precursor solution determine the features of the synthesized material. In the last years, electricity-driven hydrogen production by electrochemical splitting of water has received particular attention because of its potential applicability in decentralized energy storage concepts. Most of the efforts have been focused on the electrochemical reaction occurring at the anode side, the oxygen evolution reaction (OER), since it is source of large overpotentials.

In this context, Ba0.5Sr0.5Co0.8Fe0.2O2+x (BSCF) perovskite prepared by FSS has demonstrated to be one of the most promising materials presenting a high OER (1). In this work, the influence of the different synthesis parameters on the OER activity is shown. The concentration of the precursor solution was studied between 0.1 and 0.3 M, its pumping flow rate into the flame between 10 and 60 mL/min and the dispersing oxygen flow rate between 25 and 45 L/min. The obtained OER values are within the interval 1-10 A/g.

(1) E. Fabbri et al., Nature Materials 2017, 16: 925–931

Keywords: Flame Spray Synthesis, Perovskite, Oxygen Evolution Reaction

3- ABS 735

STUDY OF FREEZE CASTING PROCESS TO GENERATE FUNCTIONAL POROSITY GRADIENTS IN Al_2O_3 CERAMICS

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The presence of pores in ceramic materials, for a long time, was considered to be harmful, mainly in mechanical applications, and even in other applications, a minimum of mechanical strength is required, making porosity a critical factor. With the development of new technologies and with a growing need for porous materials with ceramic characteristics, a balance between porosity degree and properties began to be studied. The obtaining controlled porosity processes in ceramics materials depends basically on the morphology, distribution and pore size desired. One of the methods used to generated porosity in ceramics is the freeze casting. This process consists in freezing aqueous or non-aqueous ceramic slurries. During this process, the particles dispersed in the slurry are expelled from the newly formed solid, stacking between the ice crystals. After this process, the solvent is sublimed, producing the green bodies. The pore structure produced by this method is like a network of unidirectional channels, where the formed pores are a replica of the frozen solvent. In this study, preparation and characterization of alumina ceramic materials with functional porosity gradients using freeze casting method were performed. In order to produce samples with different amounts of porosity, it was prepared ceramics slurries with different amounts of solids. To perform the freeze casting process, a freezing system was developed for the unidirectional growth of the ice crystals. In this system, the heat withdrawal from the suspension occurs at the base of the support by cooling it in a liquid nitrogen bath. In order to have the same initial conditions for all the samples, the ceramic slurries and freezing system were kept at room temperatures until the start of the process. Porosity characteristics were investigated concerning pore morphology, pore distribution in the ceramic matrix and processing route interference in pore formation. Mercury intrusion method was used to evaluate the porosity obtained during the process. The mechanical properties, as well as the fracture mode, were investigated during uniaxial compressive test in a universal testing machine. Using the images obtained by scanning electron microscopy, it was possible to correlate the data obtained in the porosimetry analysis with the mechanical response obtained from the material. The results suggest that the porosity obtained in all samples are similar, even when varying some process parameters. When evaluating mechanical properties, these different parameters changed drastically compressive strength and failure mode. The pore microstructure and morphology obtained were pore channels highly connected.

Keywords: freeze casting, porous, graded porosity

4 - ABS 311

REVERSE OPALINE STRUCTURE OF NiO BY ELECTRODEPOSITION

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In the present work the process for the fabrication of a three-dimensional opal reverse nickel oxide (NiO) structure is shown, this three-dimensional structure contains in its interior homogeneously distributed porosities of nanometric sizes throughout its structure, this is possible by means of a membrane formed by spheres of Poly methyl methacrylate (PMMA), by means of a FCC packing generated by the evaporation of the spheres that are in a solution a colloidal glass (opal) is formed that presents interstitial voids due to the sintering by a treatment applied thermal The reverse opal is formed by vertical electrodeposition with a system of three electrodes, using as an electrode a conductive glass that was coated with ITO by means of the spin coating technique, during the process the interstitial holes found in the opal are filled. Afterwards the spheres are removed with a solvent forming an inverse opal (around the spheres), once the structure is obtained, a thermal treatment is applied, which will form the NiO inverse opal structure, for the study of the behavior of the magnetic properties in this type of three-dimensional structures.

Keywords: Opal inverse, Electrodeposition, NiO

5 - ABS 702

EFFECT OF HALLOYSITE CONTENT AND HEAT TREATMENT ONTO THE PROPERTIES OF USE OF TEXTURED KAOLIN-BASED CERAMICS

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Because of their mineralogical characteristics and their low cost, there is a renewed interest in improving the properties of phyllosilicate-based ceramics in order to use them as innovative technical ceramics.

The main objective of this work is to study the influence of the initial texture, due to the particles morphology of such natural raw materials, and the temperature of thermal treatment, on the final properties and microstructure of the resulting products shaped through by tape casting. The raw phyllosilicates materials used in this work were a kaolin and a halloysite containing particles with platelet and tubular shapes, respectively. Samples were prepared from various mixtures of halloysite and kaolin (0, 25, 50, 75 and 100 wt. %) and shaped using tape casting. The surfactants used to ensure the stability and the cohesion of the green tape are namely: dolaflux B11® as dispersant, Polyvinyl alcohol 22000® as binder and Polyethylene glycol 300® as plasticizer.

The slurries were prepared with respect to the rheological behavior required for the tape casting process. The physicochemical characteristics of the as-obtained tapes were determined together with their structural changes (XRD, SEM) upon sintering. Moreover, the effects of the firing temperature and the halloysite content on the microstructure and the mechanical and thermal properties of the tapes were investigated.

The open porosity of the various samples tended to decrease with increasing firing temperature as expected. However, the increase of the halloysite content seemed to favor a higher residual porosity within the sintered tapes regardless of the firing temperature. Besides, the thermal and mechanical properties of the green and sintered tapes were improved with increasing halloysite content and the temperature of heat treatment. These results appeared consistent with the particles morphology of the mullite within the studied samples as well as the shape of the pores. The development of such phyllosilicate-based materials with controlled microstructure seems very promising for manufacturing innovative environmentally friendly technical ceramics.

Keywords: kaolin, halloysite, tape casting, sintering, texture, properties of use

6 - ABS 673

DEVELOPMENT AND CHARACTERISATION OF MULTILAYER COATINGS VIA THE SOL-GEL METHOD

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This study is part of the Interreg TRANSPORT project. It is a collaboration between French and Belgian research teams.

The field of transport is very developed on both sides of France-Belgium border. Longevity and reliability of metal parts are key features in this sector. Existing materials are expansive, and do not meet the manufacturers main requests because they are not both corrosion-resistant and wear-resistant. For this reason, there is a strong demand for more effective and cheaper components.

The aim of this thesis is to develop ceramic multilayer coatings on metallic substrates via the sol-gel route, displaying both wear and corrosion-resistance. A multilayer coating consisting of titania is studied. These layers are deposited by dip-coating. First, a dense layer will act as a mechanical cling and a barrier in case of corrosion. Then a porous layer will be impregnated with a lubricant in order to decrease the friction coefficient.

The first step of this work has been dedicated to the optimisation of the dense layer sol-gel process. The results show that it is possible to obtain a homogeneous crack-free coating.

In the second part, a porous TiO2-SiO2 layer has been developed using a pore-creating agent: PEG. Tests carried out on glass substrates show a layer with spherical porosity. Some parameters such as PEG amount and dip-coating withdrawal rate have been more specifically studied to obtain a better porosity control. Tribological characterisations will be conducted once the porous layer would have been impregnated with a lubricant.

Keywords: multilayer coating, sol-gel method, tribology

7 - ABS 663

MAGNETRON SPUTTERING THIN FILMS WITH PREFERRED ORIENTATION FOR POSITRON MODERATION

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Positron annihilation lifetime spectroscopy (PALS) and Doppler-broadening spectroscopy (DBS) are two positron annihilation spectroscopy derived techniques suitable for identifying near surface vacancies and dislocations in lattices induced due to the positrons high affinity to volume defects. Irrespective to the method used to obtain them, positrons manifest a broad energy distribution of about several MeV. In order to use them in generating a low-energy positron beam, positrons need to be “slowed” and to achieve positron beam intensities in the range 10 (E+06) - 10 (E+07) e+ / s. The way to achieve that is by mounting a material called “moderator” in close proximity of the positron source, so that a narrow positron kinetic energy bandwidth can be obtained, without losing too much intensity. The moderator must possess certain properties, the most important being the negative positron work function. For moderation purposes, nowadays, materials with negative positron work function, e.g. single crystal W, or solid Ne are used [1][2]. GaN has shown impressive advantages due to its negative workfunction and large branching ratio which make GaN a very promising candidate for positron moderation and field assisted moderation. Because of its 3.4 eV bandgap, it might manage longer average diffusion lengths due to its epithermal positron diffusion [3].

As the rapid development in the knowledge about GaN growth techniques continues, the aim of the present study is to obtain semi-insulating GaN thin films, in a variance of parameters (such as temperature of the substrate, forwarded power, target to substrate distance, working pressure, use of gas mixtures in different percentages, DC or RF plasma) by magnetron sputtering on different substrates (Si, SiC, TiO2, ZnO, Al2O3) with fewer intentional and unintentional impurities incorporated, which should hold promises of increasing the positron diffusion length in the material.

Preliminary depositions made in this study are to be discussed, highlighting both their advantages and limitations derived from their structure characterization by X-ray Diffraction and High-Resolution Transmission Electron Microscopy coupled with EDX elemental mapping.

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Keywords: Thin films, Magnetron sputtering, Positron moderators

8 - ABS 625

THE EFFECT OF MECHANOCHEMICAL ACTIVATION OF STARTING MATERIALS TO HYDROTHERMAL SYNTHESIS OF C-S-H PHASES

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The crystalline calcium silicate hydrates are very difficult to synthesise. Most often the preparation is carried out in hydrothermal conditions using SiO2, CaO and water as starting materials. The length of the reaction depends on many factors and ranges from hours to weeks. The longest reaction step is the dissolution of SiO2. The mechanochemical activation of the starting mixture increases the reactivity and decrease the time of the hydrothermal step of the preparation of the C-S-H phases.

The main aim of the contribution is to describe two-step synthesis of the crystalline C-S-H phases, mainly a mineral tobermorite. The first step of the synthesis is the room temperature wet grinding of a mixture of SiO2 and CaO. The starting mixture with the CaO/SiO2 ratio equal to 0.83 was milled with different water amounts in a planetary ball mill. The starting materials were synthesised from pure chemicals, SiO2 via sol-gel reaction from tetraethyl orthosilicate (TEOS) and CaO by precipitation reaction from calcium nitrate. The water to solid (w/s) ratio differs from 1.5-8 ml/g. The milling time was set to 4 hours. The second step of the synthesis was the hydrothermal treatment of the dried product. All synthesis was done at 180 °C in a laboratory steel autoclave. The samples after both steps were characterized in order to determine the phase composition, which was done by X-ray diffractometry. The thermal behaviour of samples was studied by TG-DTA. Morphology and particle size of synthesized powdered products were studied by scanning electron microscopy.

Keywords: C-S-H phases, mechanochemical activation, hydrothermal reaction

9 - ABS 612

DENSIFICATION PROCESS INVESTIGATION OF NANOYTTRIA OBTAINED BY SOLUTION COMBUSTION SYNTHESIS

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In the presented work nanoyttria powder was studied in terms of its application in ceramic technology. The high-temperature self-propagating red-ox reaction between yttrium nitrate and glycine was used to prepare yttria nanopowder by Solution Combustion Synthesis (SCS). The product obtained in SCS process was characterized in terms of its microstructure, particle size distribution and BET specific surface.
In order to improve packing ability nanopowders were crio-granulated using commercial dispersants and binders. Sintering process was designed basing on dilatometric results. Samples sintered pressurelessly were than densified in Hot Isostatic Press.

Keywords: yttria nanopowder, SCS, DIL

10 - ABS 596

PHOTOCATALYTIC ACTIVITY AND STABILITY OF ZINC OXIDE-TITANIA FILMS PREPARED BY SPRAY PYROLYSIS

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Zinc oxide–titania nanostructures are considered as promising visible light photocatalysts due to better light absorption and effective charge separation. However, at present results of the studies are contradictory. The diverse influence of TiO2 on ZnO photocatalytic activity could be connected with used various preparation and testing methods as well as by reducing active surface area of zinc oxide. In the present work activity and stability of ZnO/TiO2 coatings prepared by spray pyrolysis were studied in dependence on spraying mode of precursors and content of titania.

Separate solutions of zinc acetate in ethanol and titanium isopropoxide in ethanol and acetylacetate were prepared for formation ZnO films coated with titania. The complex ZnO/TiO2 coatings were prepared by spraying mixture of the both solutions. The solutions were sprayed onto cleaned Ni foil at 400 oC using Holmarc Pyrolysis Equipment. Photocatalytic activity was determined by degradation of MB solution under Osram Vitalux lamp, 300 W (simulated sunlight) illumination and was compared with natural solar illumination.

Two types of coatings were obtained by spray pyrolysis – ZnO films coated with thin layer of titania and complex ZnO/TiO2 films using mixture of the both solutions. All prepared films had uniform surface without cracks and consisted from grains in the range of 0.1-0.4 μm. The maximal photocatalytic activity of ZnO/TiO2 coatings was reached at spraying temperature of 350-400 oC, concentration of zinc acetate solution of 0.2 M/L at flow rate of 0.1-1.0 mL/min using cyclic spraying mode – 1 min deposition followed by 3 min break.

ZnO films coated with thin layer of titania (0.2-3.5 wt.%) showed the highest activity at TiO2 content of 0.5-1.0 wt.% when degradation degree of methylene blue (MB) solution (7.3 mg/L) reached 67.5 wt.% and exceeded that of bare ZnO. Complex ZnO/TiO2 coatings reached maximal photocatalytic activity at TiO2 content of 1.0-1.5 wt.%. The further increase of the titania content in both coatings led to decrease of the photocatalytic activity. The change of MB solution temperature from 24 oC up to 34 oC increased degradation degree of MB 1.3 times. Similarly, decrease of MB concentration from 10.8 mg/L to 3.3 mg/L increased degradation degree 1.2 times. The ZnO/TiO2 coatings prepared by both spraying modes during 5 reuse cycles showed high chemical stability and some increase of photocatalytic activity.

Acknowledgements. The research was supported by ERDF project No. 1.1.1.1/16/A/079 “Development of active under sunlight immobilized TiO2-ZnO based photocatalysts”

Keywords: ZINC OXIDE-TITANIA THIN FILM,PHOTOCATALYST,SPRAY PYROLYSIS

11 - ABS 590

ELECTROPHORETIC DEPOSITION OF A METAL-CERAMIC COATING CONTAINING MCrAlY (M:Ni,Fe) BOND COAT FOR CARDIOVASCULAR IMPLANTS.

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The main aim of the presented project is the development of a reproducible, tailor-made metal-ceramic coating with hemocompatible properties for permanent medical use on cardiovascular implants with direct blood contact such as stents. In addition to hemocompatibility, the coating should increase the lifetime of the applied materials. The metal matrix provides the necessary flexibility and adaptation of the expansion to the substrate. The dispersed ceramic particles in the metallic matrix improve the hemocompatible properties of the coating.

In this work MCrAlY (M: Ni, Fe) bond coat and Al-Al2O3 top coat were applied using electrophoretic deposition and sintering. Using the electrophoretic deposition and the charging system of iodine-acetone, NiCrAlY and FeCrAlY bond coat was successfully deposited on a steel substrate. The samples were sintered in argon and vacuum (1x10-5 mbar) at range of temperatures from 1000 °C up to 1200 °C for 30 and 60 minutes. In order to improve the adhesion, the steel plates were previously sandblasted. The Al-Al2O3 composite coating was applied as a second layer by the electrophoretic deposition and the charging system of iodine-acetone and sintering, as well. To evaluate the phases formed at each temperature the XRD-analysis was performed. The morphology of the samples was analyzed by SEM and an adhesion test was executed.

In this study we could show that the MCrAlY (M:Ni,Fe)-coatings could be successfully obtained by the electrophoretic deposition by using the charging system of iodine-acetone without any other additives. It is also possible to perform the sintering in argon or vacuum atmosphere with a good adhesion to substrate. The top coat (Al-Al2O3) adheres the bond coat in a proper way. Hemocompatibility tests according to ISO 10993-4 are ongoing.

MCrAlY (M:Ni,Fe) is a trendy and promising material that can provide a good adhesion of ceramic and metal and can be applied by a simpler method like the electrophoretic deposition. It can be used not only as thermal barrier coating but also as a bond coat for ceramic coatings for medical use.

Keywords: electrophoretic deposition, MCrAlY bond coat, metal-ceramic coating

12 - ABS 585

BORON CARBIDE SYNTHESIS USING EXPANDED GRAPHITE AS ONE OF CARBON FORM

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Boron carbide is one of two known diamond-like carbides. Boron carbide, besides the extremely high hardness, has very other interesting properties like: low density, high thermal conductivity, high chemical resistance and very high neutron capture cross-section. Due to its very wide range of properties, boron carbide is used as an example: abrasive in abrasive and polishing applications, as ballistic armour; as an absorbent for neutron radiation, include BNTC (boron neutron capture therapy) cancer therapy. Such BNTC therapy application require nanometric, phase homogeneity and high chemical purity boron carbide powders synthesis. Boron carbide powders were usually synthesized by boron oxide carbothermal reduction or magnesothermic boron oxide reduction performed at high temperature (1900 – 2000Cdeg.) and the obtained product require grinding and purifying. Fine grained boron carbide powders using direct reaction between B2O3 or H3BO3 boron precursors and the organic carbon precusor like saccharose can be obtained. Such methods are time – and labour – consuming and the carbon is the main unavoidable impurity. The aim of the present paper is to study the using of the one of the carbon form - expanded graphite as the substrate for the fine boron carbide powders synthesis. Removal of the intercalating agent from the graphite structure in the exfoliation process results of the expanded graphite creation. Very rapid intercalating agent removal leads to the strongly defected graphite structure creation. Foaming graphite is therefore very lightweight and porous material. Those specific structural and microstructural composition makes the expanded graphite very high reactive carbon form. Described in the paper sythesis method of the boron carbide fine powder is very uncomplicated with the monophase product obtained at the <1600Cdeg. temperature which does not require further chemical and mechanical processing.

Keywords: boron carbide, expanded graphite, fine powder

13 - ABS 568

PREPARATION OF CHELATE FUNCTIONALIZED MAGNETITE USING AMINE CONTAINING SILANOL OR POLYMER PRECURSOR

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Genetic technology and protein technology had been focused as special area in the bio technology, so that the acceleration of separating nucleic acid and protein had been arisen one of the hottest issue. Therefore the magnetite nanoparticle with bio-attachable chemical ligand was assumed compromising candidate for the high speed separating material.
Based on the magnetite nanoparticle, amine had been attached by couple of functionalization method with polyethyleneimine(PEI) and (3-aminopropyl)triethoxysilane(APTES). Then nitrilotriacetic acid(NTA) was linked with terminal amine group via glutaraldehyde (GLA) as cross-linker.
After that, chelate attached specimens were analyzed from the electro-chemical and morphological point which were differed by chemicals used for amino functionalization.
Then it was discussed that which causes the differences and which specimen is more adequate for furthermore application.

Keywords: Magnetitie, Amino functionalization, Chelating ligand

14 - ABS 547

SYNTHESIS AND CHARACTERIZATION OF Al_2O_3/SiO_2 CORE-SHELL NANOPARTICLES THROUGH SOL-GEL PROCESS FOR LASER SINTERING APPLICATIONS

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Fabrication of 3D Al2O3 ceramic complex parts using selective laser sintering (SLS) is widely investigated recently. Most of the studies mainly focus on manufacture techniques, slurry preparation, and product properties. However, the high melting temperature of Al2O3 make it difficult to obtain high density bodies. The need for appropriate materials is critical to the selection requirements for laser sintering to reduce the sintering temperature and homogeneous densification. Our present work is to fabricate Al2O3/SiO2 core-shell nanoparticles using the sol-gel method and micro emulsion technique and to develop a solid freeform fabrication technique for the materials system by layering binder-free, high-loaded ceramic slurries, followed by selective laser sintering. The lower melting silica phase and the reaction sintering between silica and alumina favor the rapid prototyping of pure ceramic parts.

Al2O3(core)/SiO2(shell) nanoparticles were prepared from alkoxide solutions by the hybrid sol-gel method. The hybrid organic-inorganic sols with addition of tetraethyl orthosilicate (TEOS), glycidoxipropyltrimethoxysilane or phenol-formaldehyde resin were used to improve the quality and distribution of shell coating on Al2O3 powder. The synthesis of core-shell nanoparticles was performed by modifying the Stober method via the hydrolysis of TEOS in the presence of Al2O3 nanoparticles by adding ammonia hydroxide. The thickness of the SiO2 shell was controlled in the range of 5 nm to 30 nm by varying the hydrolysis conditions. The core/shell nanoparticles were characterized by X-ray diffractometry (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive Spectrometer (EDS), fourier transform infrared spectroscopy (FTIR), and thermal-gravimetry analyzer (TGA).

For the build-up of 3D structures, the powder layers were scanned by a CO2 laser with a maximum power of 60 W. It was found in laser parameter studies that ceramic parts can only be obtained using special silica contents and laser parameters. It was found that the bodies with crack-free and integrated shape under laser sintering could be obtained when the thickness of the SiO2 shell was more than 15nm. Photonic crystal geometries with strut size down to about 0.5 mm were fabricated to be denser and crack-free micro-components with optimal surface quality by using the core-shell nanoparticles.

Keywords: core shell, sol gel, laser sintering

15 - ABS 536

SYNTHESIS OF Fe_3O_4-SnO_2 CORE-SHELL NANOCOMPOSITES BY TRI-SODIUM CITRATE DIHYDRATE OR PAA SURFACE TREATMENT

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Nano-composite materials can provide a new way to overcome the disadvantages of conventional materials and can appear innovative physicochemical characteristic that will be fundamental for future technological applications. Simple strategies for manufacturing spherical nanoparticles have attracted great attention in a variety of fields, thus enabling faster development of nanotechnology. Fe3O4 nanoparticles have been used in various fields not only as promising candidates for pigments, recording materials, MRI contrast agents, electrophotographic developer, and efficient heat transfer but also as electrode material of lithium-ion battery. Fe3O4 nanoparticles are a kind of transition metal oxide that has a higher electrical conductivity than that of most of the other metal oxides. Tin dioxide (SnO2), a well-known n-type semiconductor, is another fascinating anode material for LIBs because SnO2 have high electron mobility, high theoretical specific capacity (782 mAh g-1) and large band gap (3.6 eV). In this study, The core-shell-structured Fe3O4-SnO2 nanocomposites were successfully synthesized by the simple solvothermal reaction. We propose two ways to conjugate SnO2 nanoparticles on the Fe3O4 particle surface using tri-sodium citrate dihydrate (tSCD) and poly(acrylic acid) (PAA) as pretreatment materials. Herein, tSCD and PAA effectively formed carboxyl groups on the core particles. The Fe3O4 particles surface-treated with tSCD or PAA were subject to the reaction with sodium hexahydroxostannate (NaSnO3·3H2O) in water, resulting in Fe3O4-tSDC-SnO2 and Fe3O4-PAA-SnO2 nanocomposits, respectively. The surface treatment method prior to conjugating with SnO2 nanoparticles affected the amount of SnO2 adsorbed on the Fe3O4 particle surface. Consequentially, The surface characteristics of the Fe3O4 particles surface-modified with tSCD and PAA were confirmed by fourier transform infrared spectroscopy (FT-IR, Nicolet 5700, Thermo Electron, USA). The surface charges and dispersion properties of the particles were measured using zeta potential and particle size distribution analysis (Zetasizer Nano ZS, Malvern, UK). The crystal structure and morphology of the synthesized nanocomposites were measured over the 2θ range from 20 to 80 degrees by X-ray diffraction (XRD; UltimaIV, Rigaku, Japan) with Cu Kα radiation (λ = 1.5418 Å) and high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F30 S-Twin, FEI, USA). Finally, the SnO2 content of composite surface was determined using the energy dispersive spectroscopy (EDS, EDAX detector (DPP-II), USA).

Keywords: Fe3O4-SnO2,trisodium citrate dihydrate, poly(acrylic acid)(PAA)

16 - ABS 533

PREPARATION OF TUNABLE IRON OXIDE NANOPARTICLES VIA SOLUTION COMBUSTION SYNTHESIS

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Iron oxide nanoparticles exhibit remarkable physical and chemical properties, which are used in various technological and biomedical applications. Reports indicate that the most common approach for the iron oxide preparation is the precipitation route. Although solution combustion synthesis proved to be a versatile preparation route in terms of energy-saving, processing time and powder features, there is a limited number of studies dealing with the preparation of iron oxide nanoparticles using this approach. In this study different iron oxide nanopowders were prepared by solution combustion synthesis, starting from stoichiometric mixtures (equations 1-2) of iron nitrate (III) nonahydrate (Merck) and monoethanolamine (Merck) or triethanolamine (VWR):
26 Fe(NO3)3 + 30 C2H7NO = 13 Fe2O3 + 60 CO2 + 105 H2O + 54 N2 (1)
22 Fe(NO3)3 + 10 C6H15NO3 = 11 Fe2O3 + 60 CO2 + 75 H2O + 38 N2 (2)
The influence of fuel type (monoethanolamine / triethanolamine) and reaction atmosphere (air / absence of air) on the phase composition and iron oxide properties were investigated. It was evidenced that properties of the obtained samples were quite different in terms of phase composition, crystallite size, specific surface area and magnetic features.
XRD analysis indicated that the samples obtained in the absence of air consist of maghemite and/or magnetite, having crystallite size of 11 nm (triethanolamine) and 75 nm (monoethanolamine). At the same time, the BET specific surface area was 5 m2/g in the case of sample prepared with monoethanolamine and 65 m2/g in the case of the sample prepared with triethanolamine. Larger crystallite size and smaller specific surface area of the sample prepared with monoethanolamine were consistent with the higher temperature developed during the combustion reaction. The TG-DSC investigations indicate that combustion reactions conducted in air were more exothermic than those conducted in the absence of air, which explains why samples prepared in air consist mainly of hematite.
Overall, various iron oxides with tuned properties can be prepared by solution combustion synthesis, using monoethanolamine and triethanolamine as fuels. Reaction atmosphere also plays a key-role.

Acknowledgments
This work was supported by a grant of Minister of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2016-0765, within PNCDI III.

Keywords: iron oxide, combustion synthesis, nanoparticles

17 - ABS 448

RELATIONSHIP BETWEEN CROSSLINKING DENSITY OF PHOTOPOLYMER AND VALUABLE CERAMIC CORE

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Objective In order to shorten the processing time and to improve green body strength, a photo-curable binder was used instead of an organic binder used in a conventional casting process [1]. The photopolymerization reaction is one of methods to synthesize a high-density polymer in a short period of time in which a small amount of a UV-activated photoinitiator is added to a photopolymer. In this work, acrylates with various functionalities were employed as a monomer for the photopolymer, and the relationship between the crosslinking density and the green strength was investigated.

Materials & Methods Core samples were prepared through compression molding method with a mixture of starting powder, isobornyl acrylate (IBOA) with one functionality, pentaerythritol triacrylate (PETA) with three functionalities, and 1-hydroxy cyclohexyl phenyl ketone (HCPK) as an initiator. Ultraviolet rays of 365 nm wavelength were irradiated for 30 min. IBOA and PETA were mixed at a molar ratio of 1: 1 for making the monomer with two functionalities. The inorganic binder system consisted of TEOS (SiO2 precursor) and NaOMe (Na2O precursor) was employed to enhance the strength. The green body was dipped into the inorganic binder and dried 200°C for 1 h [2]. Schematic diagram for preparing sample is shown in Fig. 1.

Results FT-IR analysis showed a peak at 1723cm-^{1} caused by acrylate. The content of initiator is shown in Table 1. As the functionality of monomer increased, less initiator was added for polymerization. Generally, a high degree of polymerization means that the crosslinking density is high. Therefore, as the functionality increases, the fracture strength will increase. Figure 2 shows the green strength according to the type of monomer. As the functionality of monomer increased, the green strength of sample was improved because the degree of polymerization and crosslinking density were increased. Especially, in the 3–functionality, the highest molding strength was obtained, compared to the conventional process in which the green strength is exhibited by the entanglement of the polymer chain. In addition, when the inorganic binder was impregnated three times, the highest strength was achieved due to the sol-gel reaction of the inorganic binder during drying process.

Conclusions A photopolymerizable polymer instead of an organic binder was applied to increase the green strength of the ceramic core. As the functionality of monomer increased, the green strength was improved due to the increase of crosslink density, that is the degree of polymerization.

Keywords: Photopolymerization, Ceramic core, Functional group

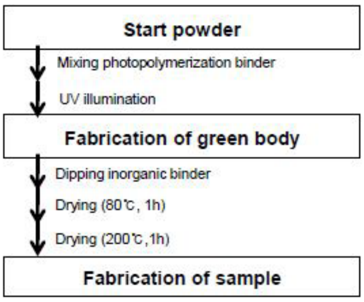

Fig. 1. Schematic diagram for preparing core samples by photopolymerization process.

Table1. The content of initiator for polymerization as a function of monomer type

Initiator	IBOA	BDDA	PETA
HCPK(mol%)	1.6	0.8	0.1

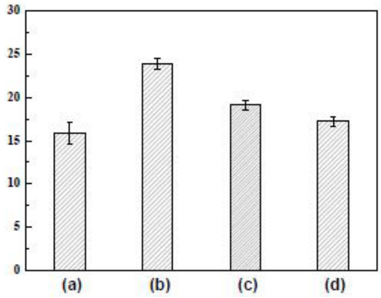

Fig. 2. Green strength as a function of funcationality: (a) PVA, (b) PETA, (c) PETA mixed with IBOA, and (d) IBOA.

19 - ABS 344

OBTENTION OF MIXED TITANIA/ALUMINA OXIDE SYNTHESIZED BY SOL-GEL WITH ELEVATED DISPERSION OF TITANIA PHASE

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Ceramic mixed oxide produced by Sol-Gel synthesis has been developed for a wide variety of applications. The aim of this study was the synthesis of mixed TixOy/ AlmOn oxide ceramic containing 10, 15 and 20% of TiO2 from metal alcoxides of aluminium and titanium. These precursors were blended using acetylacetone as a complexant agent to control the hydrolisis and condensation kinetic of titanium alkoxide. The morphological characteristics and phase composition of mixed oxides obtained were evaluated by X-Ray diffraction, energy dispersive X-Ray, scaning electron microscopy, differential scaning calorymetry, BET surface area and particle syze by dynamic light scattering. The XRD patterns show that the mixed oxide obtained consists of boehmite and anatase. Except by the composition where was expected an amount of 10% of the TiO2 the amount of TiO2 in relation of amount of alumina obtained was the projected. The Rietveld analisys applied over the XRD patterns shows that the mixed oxide formed had a low crystallinity and that the increase in amount of TiO2 precursor led to a growth of the crystallite size of titania and a decrease of the crystallite size of boehmite. It could be explained by a faster coalescence of TiO2 crystals or by influence of OH- ions in the reaction medium that would preferentially connect to Ti cations than to Al cations favoring the growth of the anatase crystals in detriment of the boehmite crystals. DSC curves show that as anatase content was increased in the mixed oxide the transformation of boehmite in alpha alumina was decreasing, until at a content of 20% of anatase no transformation was observed. The lower transformation of boehmite into alpha alumina and the reduction of boehmite crystallite size, indicate that the increase of anatase content in precipitated mixed oxide has influence on the boehmite crystallization mechanism. The analyse of morphology of the lyophilized mixed oxide shows large, fairly flat agglomerates of various sizes and geometric shapes. Surface roughness in agglomerates could be observed at higher magnifications and these superficial irregularities indicate the existence of smaller structures, forming large particles. The high dispersion of the Al and Ti chemical elements is observed in all analyzed samples indicating that the hydrolysis and condensation rates of aluminum and titanium precursor alkoxides were controlled by the use of the complexing agent acetylacetone. The particle size varied in a range of 130 to 200 nanometers and the lowest value was obtained for the mixed oxide with a content of 20% of anatase. The surface area for all compositions was around 250 m2/g. So the route used was adequate to obtain the TiO / AlO mixed oxides with a high dispersion of the anatase phase in boehmite, high surface area and nanometric particle size.

Keywords: Sol-Gel Syntheses, Mixed Ceramic Oxides

20 - ABS 293

SYNTHESIS AND CHEMICAL LIXIVIATION OF NANOSTRUCTURED CALCIUM-DOPED MAGNESIUM ALUMINATE SPINEL

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The study of sintering additives is very important to understand the mechanisms which can decrease sintering temperatures, especially in important technological materials, such as Magnesium Aluminate Spinel (MAS). These additives usually are introduced during synthesis step. In this work, nanometer powders of magnesium aluminate will be synthesized by reverse coprecipitation. Pure and doped Ca ^{2}+ doped MAS powders were obtained using different concentrations (varying from 0.2 to 2.0 mol %) and temperature calcinations (from 700 to 900°C). Chemical analysis by XRF was coherent with nominal addition and, calculated grain boundary area suggested preferential segregation at solid-solid interfaces. Surfaces specific area between 90m^{2}/g and 150m^{2}/g and crystallite size about 10nm (and below) indicates that a nanostrucured powder was obtained. The powders were subjected to chemical lixiviation process, which is able to remove possible carbon contaminations (common in nanostructured oxides), and some segregated additive on nanopowders surfaces. The evolution of macroscopic characteristics of these powders were investigated, focusing on area of solid-solid interfaces, which are very important during sintering.

Keywords: Magnesium Aluminate Spinel, Chemical Lixiviation, Grain Boundary

21 - ABS 285

STUDY OF SOLUTION COMBUSTION SYNTHESIS OF YAG BY DIFFERENTIAL THERMAL ANALYSIS

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In the presented work Solution Combustion Synthesis (SCS) induced by microwaves was used to obtain yttrium aluminum garnet nanopowder. During the reaction nitrates oxidize reducing agent to form metal oxide and gaseous products and the overall reaction can be described by the following equation:
3 Y(NO3)3 + 5 Al(NO3)3 + „reducing agent" --> Y3Al5O12 + x CO2 + x H2O + x N2
In the presented work reaction of nitrates with urea was investigated. Decomposition process of the nitrates, urea and their mixture was examined using differential thermal analysis coupled with analysis of evolved gases composition by FT-IR spectrometer.
Powders obtained in the reaction were tested for sinterability using high-temperature dilatometer.

Keywords: DTA-FT-IR,YAG nanopowder, Solution Combustion Synthesis

22 - ABS 166

RAPID THERMAL DEBINDING OF INJECTION MOLDED SiC CERAMICS IN OXIDATIVE ATMOSPHERE

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Powder injection molding (PIM) is an efficient method for the fabrication of silicon carbide ceramic articles. Its wide usage is caused by the advantages in production of complex-shaped SiC parts, possibilities of green machining, high quality of the obtained ceramics and relatively easy scaling.

One of the most critical stages in the PIM process is the complete removal of thermoplastic binder from the molded preform since main defects in the preform appear at this stage. For this purpose, microwave treatment, supercritical debinding, solvent extraction, catalytic debinding are used but thermal debinding is most popular and simple method. Slow heating of the molded preform (0.1–1 °C/min) is generally applied to suppress defects formation, but it cannot guarantee integrity of preform, preservation of shape and sufficient stiffness of green ceramics.

In this work, the method, on the basis of non-stationary heating model of molded parts, for rapid and efficient thermal debinding in kaolin backfill is developed. Measured thermal characteristics of all components (kaolin, paraffin wax binder, silicon carbide) were used in calculations. Kaolin powder serves as a heat damper with thermal conductivity (0.06 W/(m K)) it is less than the molded preform body (5 W/(m K)). The model results enable to define maximal heating rates for different sizes of green ceramic parts.

Green SiC ceramic parts with diameter till 200 mm and thickness till 50 mm were molded. Slow thermal debinding (10-15 h) in air (200 °C) and inert atmosphere (300–400 °C) doesn’t provide the satisfactory state of green ceramics. Using the modeling results, rapid thermal debinding in air was developed with the heating rate of 5-10 °C/min up to 600 °C and the exposition time of 2 h. Defectless green parts were obtained with enough stiffness for the further processing. It was shown that pre-sintering of SiC particles occurs to some extent due to formation of surface oxide films. The temperature of 600 °C was found to be optimal, lower temperature leading to decreased stiffness of the preform, while higher temperature results in reduced characteristics of final SiC ceramics.

Described method of thermal debinding is the part of the developed technology of the production of reaction sintered Si/SiC composite, which is highly densified (3.13 g/cm3) and has advanced combination of thermal and mechanical properties (elastic modulus up to 450 GPa, thermal conductivity ~200 W/(m K)).

This work supported by the King Abdulaziz City for Science and Technology (Saudi Arabia).

Keywords: silicon carbide ceramics, thermal debinding

23 - ABS 159

SINTERING OF DENSE POLYCRYSTALLINE GADOLINIUM- IRON GARNET ($Gd_3Fe_5O_{12}$)

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In the recent years many scientists have focused on the topic of ceramic oxide materials containing iron, due to their unique magneto-dielectric properties. These materials may hold various cations in their structure, each of them with different properties, which may translate to a broad spectrum of applications. The main advantage of magnetic ceramics, in comparison with their metallic counterparts, is that they are electric isolators. This property is key for maintaining low eddy currents losses, therefore allowing these materials to be applied in cases where these losses have to be minimized. To reach such properties such materials must be almost fully dense, with clear boundaries and narrow grain size distribution. The potential applications of gadolinium-iron garnet (Gd3Fe5O12, GdIG) may be in various types of amplifiers in microwave devices, circulators and isolators. It should be noted, that there exists a magnetization curve dependent on the temperature between the compensation point and the Curie temperature, where magnetization is approximately constant, which may be utilized in specific microwave devices.

The aim of this work was preparation of dense polycrystalline GdIG by reaction sintering with solid-state reaction between precursors of corresponding compounds of gadolinium and iron. Both precursors, hydroxides, oxyhydroxides or hydrated oxides, were obtained by precipitation from nitrates (gadolinium and iron, respectively) by ammonium solutions. Prepared powders were drained, dried and gadolinium precursor was calcined at 700°C for 1h. Stoichiometric mixture of the powders was homogenized in attritor mill for 30 minutes in ammonium solution (pH=12). The powder mixture was dried and then the cylindrical pellets were pressed uniaxially and next isostatically at 250 MPa . The compacts were sintered at temperatures from 1100°C to 1350°C for 2h. It was stated that density and grain size distribution were significantly corelated with sintering temperature. For some samples, elimination of residual porosity and preparation of fully dense materials was achieved by hot isostatic pressing (HIP) at 1200°C for 2h under argon atmosphere.

M.Stan has been partly supported by the EU Project POWR.03.02.00-00-I004/16.

Keywords: GdIG, Reaction sintering, Polycrystalline garnet

24 - ABS 145

PREPARATION AND PHOTOCATALYTIC APPLICATION OF TiO_2 FILM COATED ON ALUMINA FOAM

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Ceramic foams are lightweight materials with open or closed cellular structure. Due to their specific properties such as low density, high chemical and temperature resistance, pore interconnectivity and permeability, ceramic foams have found a wide range of applications, e.g. catalyst supports, molten metal and hot gas filters, thermal insulators, biomedical implants and lightweight structural components. In the present work, TiO2 film was deposited on alumina foam substrate by sol-gel technique. Firstly, alumina foam was prepared by the replica method in witch polyurethane sponge with a pore density of 17 ppi (pores per linear inch) was used as a template. Polyurethane template was repeatedly immersed in an aqueous alumina suspension containing 60 wt. % solid and following additives: commercial carbonic acid based polyelectrolyte Dolapix CE 64 as a dispersant, polyvinyl alcohol as a binder and Foamaster MO 2111 as a defoaming agent. After each immersion, centrifugation was conducted and the sample was dried to remove the excess suspension and to provide uniformly coated structure. Finally, a ceramic replica of the polyurethane template was obtained by pyrolysis and sintering. The slow heating rate of 1 °C/min to 600 °C and 5 °C/min to 1600 °C was applied to burn out the organic materials without collapsing of the structure. The sintering process was completed by holding the sample at 1600 °C for 1 h. For the preparation of TiO2 sol, the following components were used: titanium (IV) isopropoxide as the titanium precursor, propanol as a solvent, nitric acid as a catalyst and acetylacetone for complexation. The coating process was performed by dipping 17 ppi alumina foam into TiO2 sol followed by drying in an air oven at 80 °C. The coated sample was calcined at 500 °C for 1h. Crystal structure of TiO2 and alumina were identified by X-ray diffraction and the morphological features of the TiO2 coated alumina foam were characterized with a scanning electron microscope. The photocatalytic activity of the TiO2 film was evaluated by the photocatalytic degradation of synthetic Congo Red dye with UV light radiation at 25 °C. Photocatalytic activities of the films were monitored by means of UV/VIS spectrophotometry and total organic carbon measurement and results show the dye was efficiently degraded. Finally, the as-derived titania-alumina composite foam may be considered as valuable photocatalytic substrate.

Keywords: Alumina foam, sol-gel TiO2, Photocatalysis

25 - ABS 48

SINTERING AND PREPARATION OF POLYCRYSTALS YTTRIUM-IRON GARNET BY THE REACTION SINTERING OF YTTRIUM IRON PEROVSKITE AND HEMATITE

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Materials with the garnet-type structure have been arousing great interest. A very interesting group of materials with a garnet structure are those containing metals with ferromagnetic properties, mainly iron. Their basic properties, in contrast to pure metals, is low electrical conductivity. That property has a significant impact on low values of losses associated with eddy currents and is one of the main reasons why ceramic magnetic materials are used in areas where these losses must be minimized.

The yttrium-iron garnet (Y3Fe5O12, YIG) is one of the most important material with the ferromagnetic properties. It can be used as a basic material in microwave, acoustic, optical and magneto-optical applications. Various applications of the YIG material are a consequent of its excellent electromagnetic properties, including low dielectric losses. Moreover, dielectric losses are strictly depend on microstructure of the material, level of a porosity, grain size distribution and state of grain boundaries.

The aim of this work was to obtain polycrystalline yttrium-iron-garnet material YIG by a reactive sintering method based on a solid state reaction between yttrium-iron perovskite (YFeO3) and iron oxide, α-Fe2O3. The first step was to obtain a powder of the perovskite phase from iron and yttrium nitrate solutions with citric acid, where the ratio of total yttrium and iron to citric acid was 1:2. The mixture was dried at 100°C for 24 hours, then at 200°C for 3 hours, and finally calcined at 750°C for ?h. Aa received powder with stoichiometric addition of iron oxide was homogenized in attritor mill in an alkaline environment. The powder mixture was dried for 24 hours at 100°C and cylindrical pellets and were pressed uniaxially and then isostatically at 250 MPa. The compacts were sintered at 1450°C for 2 hours to obtain a material without open porosity. Elimination of residual porosity was achieved by hot isostatic pressing (HIP) at 1350°C for 2h under argon atmosphere. Relative density of samples sintered at 1450°C was 96.90 +/- 0.45%. The hot pressing process (HIP) caused complete elimination of porosity and a relative density of the obtained samples was 100% within the limits of measurement error. The microstructure analysis of obtained samples was carried out with use of SEM studies.

This work was supported by the National Science Centre in Poland as part of grant no. 2017/27/N/ST8/01687.

Keywords: Yttrium Iron Garnet, Reaction Sintering, Polycrystalline garnet

26 - ABS 47

TETRAGONAL ZIRCONIA-YTTRIA POLYCRYSTALS MODIFIED WITH THE ELONGATED ZIRCONIA PARTICLES

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It is well recognized that yttria forms solid solutions with zirconia. Sintering of zirconia powders with 3mole% yttria added are well known as zirconia tetragonal polycrystals characterized by the good mechanical properties, especially high fracture toughness and strength. In case of zirconia-yttria system the starting powders are usually prepared by the co-precipitation of amorphous gel using the relative aqueous salt solution introduced to the solution of the alkaline reagent, e.g. ammonia. Such gels calcined at moderate temperatures transform directly to the Y₂O₃-ZrO₂ solid solution. In the present study different processing method was applied.The starting aqueous ZrOCl₂-YCl₃ solution was introduced to the NH₃ aqueous solution. The co-precipitated gel was washed with distilled water until no reaction for Cl- ions with AgNO₃ occurred. Such gels were subjected to the hydrothermal treatment at 240^oC for 4h under autogenous water vapour pressure. It allowed us to prepare the Y₂O₃-ZrO₂ solid solution powders of nanometric (up to 10nm) and isometric particles of 3.5, 5 and 8mole% Y₂O₃ content. The elongated pure zirconia powder was manufactured by the amorphous gel precipitated with ammonia from the ZrOCl₂ solution. The gel was washed with distilled water in order to remove NH₄Cl, the byproduct of the reaction, treated several times with 4M NaOH solution and finally subjected to the hydrothermal treatment (again at 240^oC for 4h). This procedure results in the elongated zirconia particles of about 200nm length and 20-40nm thickness. The X-ray diffraction, specific surface area measurements and TEM observations were used to characterize the powders.

Mixtures of the yttria-zirconia powders and elongated pure zirconia particles were homogenized by the vigorous ultrasonic stirring of their suspensions and freeze drying. The latter treatment results in powders composed of extremely soft agglomerates. Diversification of the powders of isometric and elongated particles ratio was so that the mean final composition of the systems corresponded in each case to 3mole% Y₂O₃ content. Such powder mixtures were compacted by isostatic pressing (250MPa) and were used to study their sintering behaviour using dilatometric measurements. Phase composition changes at different densification state were studied by the X-ray diffraction. It allowed us to characterize chemical and phase homogenization of the systems.Dense samples were used to characterize their strength, fracture toughness and relate these properties to the materials microstructure.

The work was financially supported by the Polish National Science Centre under grant no 2017/25/B/ST8/02017

Keywords: hydrothermal crystallization, zirocnia yttria polycrystals, shape of zirconia particles

27 - ABS 582

REACTIVE SINTERING OF ZIRCONIUM TITANATE MATERIAL ($ZrTiO_4$) BY MICROWAVE SINTERING (MW)

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In the actuality, zirconia based materials have been developing as new composites in the ceramic field because of the mechanical and thermal properties. That is the case of the zirconium titanate (ZrTiO4). This material has been used in electro-ceramics as sensors and in the catalysis field. In the recent years, this material showed that has structural components, because of his anisotropy in the thermal expansion, also has high surface area, thermal stability and excellent dielectric and acid property.

Nowadays, developing new generation of nanomaterials with microstructural differences is necessary to innovative in the sintering process. On previous researches, the sintering process for the zirconium titanate had been made by conventional, presenting values above the 80% of densification. To have a better material, it is necessary to expose the green and compact material through different temperature processes with dwell times that can take up to 16 hours.

One promising method to produce high dense materials is the Microwave sintering (MW) that is a reactive sintering technique. This process allows working at higher heating rates in reduce dwell times (approx. 40 min) and lower consumption using 70%-80% less energy therefore reduce cost. For that reason, this process is a clearly alternative for conventional methods. Consequently, this economic aspect makes microwave more attractive from an industrial point of view.

The aim of the present work is prepare a wide of X-ray analysis by Rietveld and a microstructural characterization; developing new ceramic materials based in ZrTiO4 sintering by conventional (CS), microwave sintering (MW), and compare their properties.

Keywords: Reactive sintering, Microwave sintering, Zirconium titanate (ZrTiO4)

28 - ABS 653

DEBINDING STEP OPTIMIZATION DURING CO-FIRING OF $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSCF) ASYMMETRIC MEMBRANES MANUFACTURED BY SEQUENTIAL TAPE CASTING

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Objective Asymmetric ceramic membranes consisting of a thin dense layer supported on a thick porous substrate are considered a promising technology for high temperature oxygen separation. Tape casting is well known as a large-scale and cost-effective manufacturing technique for planar ceramic structures, and can be successfully employed to fabricate asymmetric membranes. A debinding and sintering process is always required on the green bodies produced by tape casting, to get rid of organics and achieve the desired microstructure. The purpose of this work is to investigate the effect of different debinding and sintering steps on the microstructure of asymmetric samples prepared by sequential tape casting.

Materials and Methods Asymmetric La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF) membranes were realized by sequential tape casting. Two different LSCF-based slurries were prepared for the membrane layer and the porous support. Asymmetric green tapes were achieved by casting first the dense layer and then, on the top of it, the support. The two-layered samples were debinded and sintered by co-firing in air atmosphere. During the debinding step, a forced air flow was maintained in the furnace chamber.

Samples microstructure has been investigated by SEM.

Results The co-firing process must be carefully controlled in order to achieve the proper microstructure in both membrane and support layers. Different debinding ramps were tested in which the organics vaporization rate was varied, either by changing the sample heating ramp or the volume air flow in the furnace chamber, and the maximum vaporization rate to obtain defect-free samples was estimated.

The first debinding tests were performed on samples containing the same amount of organics. A too fast debinding led to defects formation on membrane layer (Figure 1a), while defect-free samples were obtained by properly slowing the process (Figure 1b). Moreover, the same debinding step giving defect-free samples caused defects in samples containing an higher organics amount. The results described above show that the vaporization rate of organic components during debinding is a crucial parameter to avoid the formation of defects in the membrane layer or, in the worst cases, the destruction of the samples.

Some preliminary scale-up tests of co-firing processes were also performed.

Conclusions Asymmetric LSCF membranes manufactured by tape casting were successfully debinded and sintered by co-firing. A procedure was developed to estimate the maximum permissible heating rate of samples during debinding, depending on the mass of processed green tapes, the organics fraction and the supplied air flow.

Keywords: Tape casting, LSCF Membranes, Co-firing

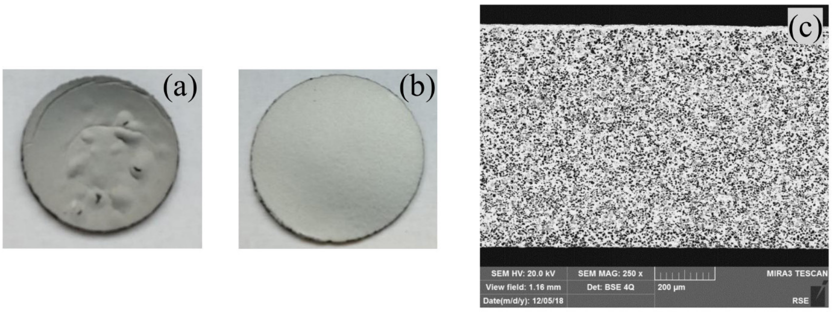

Figure 1 Asymmetric LSCF membrane samples debinded by a high (a) and a slow (b) debinding rate. (c) shows the SEM cross-section image of a properly co-fired sample.

29 - ABS 617

OPTIMISING FLASH SINTERING OF SILICON CARBIDE CERAMICS

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The application of a moderate electric field over a ceramic compact at elevated temperatures gives rise to the phenomenon known as Flash Sintering. At a critical combination of field and temperature, a power spike through the sample results in rapid densification, on the order of seconds compared to the hours taken by more conventional manufacturing techniques. This “flash event” is now largely attributed to thermal runaway, and results in rapid Joule heating as the current flow through the sample increases. The electrical and thermal properties of Flash Sintering have been successfully predicted in many materials, with the bulk of the literature concerning ionic conductors. Non-oxide semiconductors have also been shown to flash sinter, though under more extreme conditions than those encountered in typical flash sintering experiments on ionic conductors. However, they have important engineering applications and the manufacture of non-oxide materials via flash sintering warrants further investigation. Silicon carbide is such a material that is of interest in the industrial sector. A new experimental set up has been developed that allows optical visualisation of the Flash Sintering of SiC samples, in both disc and bar geometries. Liquid phase sintering aids, alumina and yttria were used, the amount and composition of which were varied. Investigation into the effects of sintering atmosphere and electrode material/geometry showed plasma formation between the electrodes under some conditions. This was detrimental to sintering. The electrical and thermal properties of SiC samples while flash sintering were investigated for different processing conditions. These were used to compare the observed conditions for the flash event with models for the process and to develop strategies for avoiding the severe current localisation which occurred under some conditions. The dependency of final sample density and microstructure on initial voltage, current density, furnace temperature and sintering time are reported.

Keywords: Flash Sintering, Silicon Carbide

30 - ABS 556

MICROSTRUCTURE OF TRANSLUCENT SILICON NITRIDE CERAMICS BY SPARK PLASMA SINTERING

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Objective Polycrystalline translucent silicon nitride ceramics are receiving a great attention in a special optical application owing to its high mechanical strength and thermal/chemical stability. To achieve the translucency of silicon nitride ceramics, highly-densified sintered bodies with a small grain size and a low content of sintering aid are required to reduce the light scattering by pores, grains and grain boundary phases. The spark plasma sintering (SPS) is available to obtain the fine-grained microstructure because of high heating rate and short-time sintering.

Materials & Metods Fine silicon nitride powder with high purity was used to achieve high density and translucency of sintered bodies. The binary additives of aluminum nitride-magnesia, aluminum nitride-yttria and alumina-yttria systems were added at a SiAlON-forming composition with a total content of 2 wt% or 12 wt%. All the samples were sintered at 30-50 MPa and 1850 deg C for 5 min in nitrogen. The heating rate was 100 deg C/min. The translucency of sintered body was evaluated in the visible light region of 400-900 nm.

Results In the present systems, a liquid-phase sintering mechanism is expected by involvement of impurity silica and alumina with magnesia or yttria. The sintered density was over 98 %. The grain size was 300-700 nm. When the additive content was large, alpha-SiAlON formed in aluminum nitride-magnesia and aluminum nitride-yttria systems, in which aluminum, magnesium and yttrium were dissolved inside silicon nitride grains. Therefore, the difference in refractive index between grain and grain boundary phase was reduced, resulting in high translucency. On the other hand, beta-SiAlON formed in alumina-yttria system without translucency, in which aluminum was dissolved inside grains but yttrium was not. When the additive content was small, beta-silicon nitride formed in all systems, and exhibited high translucency because the grain boundary was thin. The visible light transmittance increased with increasing wavelength because light scattering is weakened at long wavelength according to the Mie scattering theory, and reached 20-28 % at 900 nm.

Conclusions The SPS process is useful to obtain translucent SiAlON and silicon nitride ceramics, but appropriate sintering aids are required. Alpha-SiAlON exhibited high translucency, but beta-SiAlON did not. Beta-silicon nitride ceramics were obtained at a small additive content. Since the refractive index of silicon nitride is high, the addition of highly refractive components, e.g. aluminum nitride-magnesia or yttria is effective to reduce the light scattering by grain boundary phases.

Keywords: silicon nitride, translucency, spark plasma sintering

31 - ABS 490

HIGH TEMPERATURE WETTABILITY OF THE ALUMINOSILICATE MATRIX THROUGH THE LIQUID PHASE FROM FLUXES

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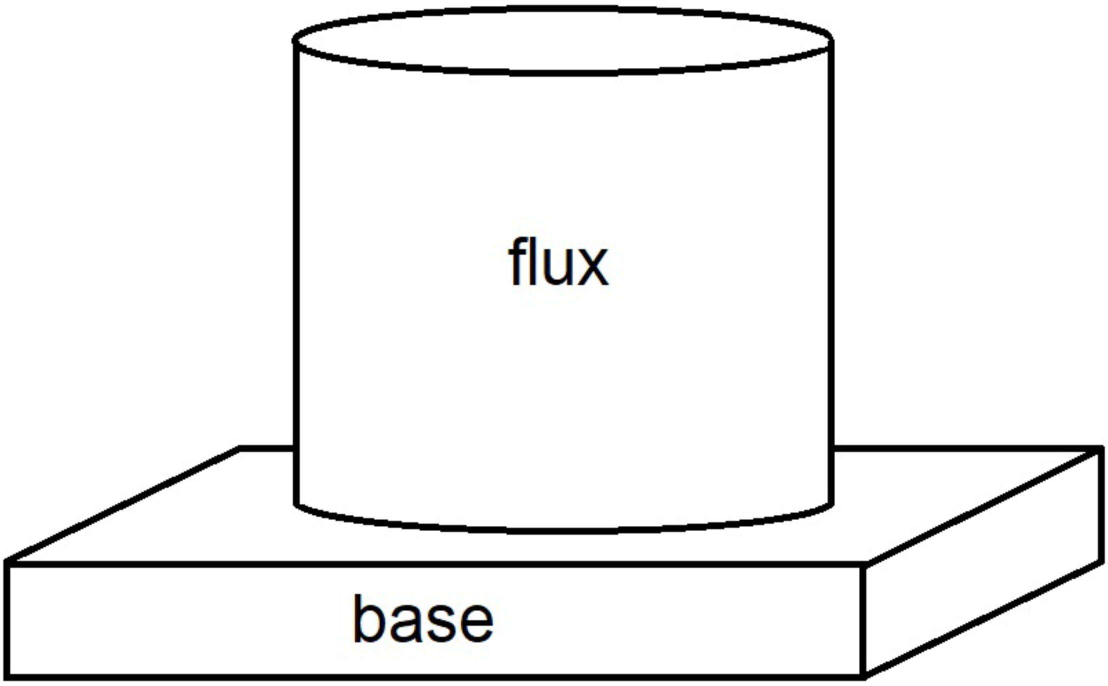
Liquid phase sintering is the dominant type of sintering occurring during firing of porcelain, sanitary and construction ceramics. The sintering mechanisms depend on its properties (ie its wettability and solubility of the solid, viscosity, reactivity with the solid) and its amount and distribution in the sintered system. In the scientific literature, there is no comprehensive study on the formation of a liquid phase in the mineral additive - aluminosilicate matrix systems typical of these types of ceramics. This paper presents the behavior of the liquid phase during heating of the flux - aluminosilicate matrix systems and its wettability of aluminosilicate matrix.

As aluminosilicate matrix kaolinite raw materials were used. They differ in the content of kaolinite, quartz and illite, which makes their sintering temperatures different. The following raw materials were used as fluxes in the form of flour: feldspar, nepheline syenite, limestone, dolomite, magnesite, bentonite, talcum and chalk. These are raw materials commonly used in the ceramic industry, but their interaction with the aluminosilicate matrix has not been fully understood.

The work presents the physicochemical characteristics of the raw materials used (chemical, mineral and grain size composition), their thermal characteristics (thermal analysis, high temperature microscopy of individual raw materials) and high temperature microscopy of flux - aluminosilicate matrix systems (in this abstract constituting a ‘base’). General scheme of the analyzed flux - aluminosilicate matrix systems is shown in the picture. These tests was allowed to determine the temperature of formation, wettability and the amount of liquid phase in the flux - aluminosilicate matrix matrix systems. There were differences in the behavior of the liquid phase depending on the used flux and kaolinite raw materials.

Keywords: High temperature wettability, Fluxes, Kaoline



32 - ABS 398

MORPHOLOGICAL AND PHASE COMPOSITION OF FILMS OBTAINED FROM THE PRODUCTS OF LASER ABLATION OF TiN-TiB_2 CERAMICS

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In the work considers the process of laser treatment of TiN-TiB2 ceramics in air. It was been established that the development of high-temperature processes in the irradiation zone (T > 2000 °C) is accompanied by the decomposition of TiN and TiB2 [1-3] into TiNx, TiB, Ti and B and the formation of vaporous ablation products, which are oxidized to TiO2 and B2O3, depending on the flight path (Fig.1). The presence of a temperature gradient in the span zone determines the interaction of the components and the formation of TixByOz compounds. As a result of the deposition on the substrate of these products from different temperature zones, the nano-coatings of various types can be obtained: a continuous glassy layer, a glassy island and in the form of a layer of TixByOz nanoparticles, TiO2 (rutile and anatase) and TiOx (Fig. 2). The results indicate the promise of obtaining films for various purposes by laser ablation of refractory ceramics by changing the distance from the ablation source (ceramics) to the substrate.

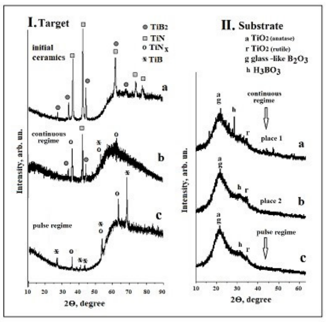

Fig. 1. Fragments of diffraction patterns of ceramic surface and its transformation after laser treatment (I) and precipitated on substrate products of ablation (II).

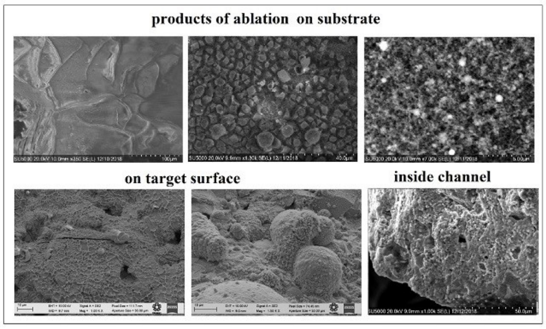

Fig. 2. SEM micrograph of ablation products precipitated on the substrate, the surface of ceramics and formed inside the crater.

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Keywords: TiN-TiB2 ceramics, Laser treatment, ABLATION PRODUCTS

33 - ABS 956

STUDYING THE MECHANISM OF REACTIVE INFILTRATION OF SILICON AND EUTECTIC Si-Zr ALLOY IN CARBON USING INNOVATIVE LASER-ABLATED MICROCHANNELS AND RADIOGRAPHY EXPERIMENT

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The reactive infiltration mechanism of molten silicon and a eutectic Si-8 at. pct Zr alloy in vitreous carbon microchannels was investigated by radiography. The microchannels were manufactured by making 20 to 100 micron deep grooves on vitreous carbon plate by laser ablation technique and clamping it with another flat plate. The extent of infiltration was observed nondestructively by X-ray radiographs. SEM and EDX were used to study the reaction layer at the interface.

The innovative technique allowed studying the mechanism of reactive infiltration in very long micron size capillaries. In addition, the effect of tortuosity can be easily studied by changing the geometry of the microchannels. X-ray radiographs not only provided the information about the extent of infiltration in the microchannels but also gave some ideas about change in reaction product along the length of the microchannel.

Keywords: Infiltration, Si-Zr alloys, Radiography

34 - ABS 308

TWO-STEP FLASH SINTERING AT 3% MOL YTTRIA-STABILIZED ZIRCONIA: AN IMPROVEMENT OF THE MICROSTRUCTURAL HOMOGENEITY

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In the last decade, the flash sintering technique (FS) was presented in the literature. This technique was distinguished by sintering materials in a few seconds at temperatures much lower than conventional ones. Several works proposed changes in FS in order to improve their results, such as Two-Step Flash Sintering (TSFS). The TSFS consists in the application of two step of electric current densities in the FS process. In the first step, a higher intensity electric current is applied for a few seconds to activate the densification mechanisms of the sample. At the second step, an electric current of lower intensity is applied to densify the material with low grain growth. In this way, the present work aims to automate the control of FS parameters such as the electric current density. For this, a tubular furnace was adapted to perform FS and TSFS. The furnace setup consists in: a displacement sensor, used to measure linear retraction; a valve system and pneumatic cylinder, used to apply a pressure of 0 to 10 bar; an S type thermocouple, attached to the side of the sample to measure the temperature in the vicinity; and an electric field application system, from platinum electrodes and a 750 W power supply. In addition, a control software was created in language and programming environment LabVIEW 2013 with routines that allow automatic control of the electric variables in real time (data refresh rate of 322 ms). We used 3 mol% of Yttria-stabilized zirconia (3YSZ) cylindrical samples (5 mm height and 6 mm diameter) shaped by isostatic pressing at 200 MPa. The samples were sintered by FS and TSFS using a heating rate of 20°C.min-1 and an electric field of 120 V.cm-1 (RMS basis), alternating current with a frequency of 1000 Hz in a sinusoidal waveform was used. For the TSFS experiments we used 100 mA.mm-2 as a maximum density current at the first step with 5 s dwell time. Then 75 mA.mm-2 for the second step with 55 s dwell time. For the FS experiments the samples were sintered using an electric current density of 100 mA.mm-2, with a dwell time 60 s. For evaluating the microstructure, the samples were polished and thermally etched. The Scanning Electron Microscopy (SEM) images reveal that the microstructure of the 3YSZ sintered by the TSFS technique was more refined and with a more homogeneous grain size distribution when compared to the microstructure of the FS sintered sample. Thus, it is concluded that the automation of the process from the creation of a supervisory software allowed the implementation of the TSFS technique and the results suggest a more refined control of the microstructure of 3YSZ from the control of the electric current during the flash phenomenon.

Keywords: Field Assisted Sintering,3YSZ,Current Assisted Sintering

35 - ABS 290

PROPERTIES OF SiC/W COMPOSITES

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The aim of the research work was to develop dense composites of negligible porosity consisting of a SiC matrix with the addition of tungsten in the amount from 1 to 8 percent by weight. The preparation of SiC/W composites was carried out with the use of granules from SiC submicron powders and W powders of various grain sizes. Reaction sintering between silicon carbide (SiC) and tungsten was used to obtain dense SiC/W materials. The SiC/W composites obtained were characterized in terms of density, hardness, microstructure, phase composition, thermal expansion, specific heat and thermal conductivity.

Keywords: SiC/W composites, reaction sintering, Hot Isostatic Pressing

36 - ABS 272

FLASH SINTERING OF 3Y-TZP/Al_2O_3 COMPOSITES

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The flash sintering technique was first reported in 2010. It consists in the conventional sintering combined with application of an electrical field, promoting the consolidation of ceramics in very short time and allowing obtention of fine microstructures in temperatures relatively lower than conventional sintering. This work presents the initial results of the effect of flash sintering on 3Y-TZP reinforced with 5 and 15 vol% of Al2O3. The powder mixtures were obtained by ball milling. 8 mm-diameter cylindrical shape specimens were pressed uniaxially and isostatically at 200 MPa. Sintering was performed in a tubular vertical furnace, adapted with an AC/DC power supply. The specimens were sintered at a heating rate of 20°C/min and electrical fields were initially set at 150 V/cm and 200 V/cm, using AC (1000 Hz) and DC, applied during the heating cycle. Sintered samples were characterized by apparent density measurements and scanning electronic microscopy (SEM). Results showed start of densification at temperatures as low as 785°C, attaining shrinkage over 20% in 15 s, for the composite with 5 vol% Al2O3 sintered with 200 V/cm DC. Relative densities varied between 79.4 and 94.6%TD. SEM results showed that refined microstructures of submicrometric grains were obtained, with some level of microstructural heterogeneity. In general, AC electrical fields allowed higher linear shrinkage than DC fields. It can be concluded that the flash sintering technique is an interesting option for rapid consolidation of 3Y-TZP/Al2O3 composites.

Keywords: flash sintering, zirconia, alumina

37 - ABS 77

THE HYDROTHERMAL SINTERING FOR LOW TEMPERATURE DENSIFICATION OF SILICA AND ANATASE

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The mastery of sintering processes is a key for the development of new high performance ceramics. Currently most of advanced ceramic materials are fabricated from powders and sintered above 1000°C to reach at least 95% of their theoretical densities. The implementation of pressure or fast heating routes or the use of nanopowders as starting materials allow to decrease these processing temperatures. However, they remain high and may appear as technological barrier to overcome. Then it appears clearly that an indisputable breakthrough in the sintering approaches would consist in combining pressure (below 350 MPa) and low temperature (at least below 500°C to avoid solid state diffusion and prevent grain growth or phase transition and/or decomposition) to densify high performance ceramics with at least 95% of compactness. The strategy is then to reproduce natural processes such as biomineralization where the formation of ceramic-dense materials such as limestone naturally occurs through large scale geological processes. Here the basic physico-chemical mechanism may involve dissolution-precipitation process, referred to pressure solution creep in geology.

In the hydrothermal sintering process, a powder with water is externally and mechanically compressed in an autoclave, under hydrothermal conditions (T between 100 and 350°C; P between 22.5 and 350 MPa) over short periods of time (from a few minutes to a few hours). The main driving force of such a process is the stress gradient within grains induced by external compression which allows the activation of the dissolution/precipitation phenomena at the solid/liquid interface. Here, water both acts as a solvent and a mass transport medium, and certainly enhances creep at the solid/solid interface to promote densification. Thus, this process promotes surface chemistry phenomena in a hydrothermal solvent, as diffusion processes in the solid phase are unexpected at such low temperatures.

We have focused our work on two nanometric or submicronic model systems: amorphous SiO2 and TiO2 anatase particles. The challenge is to perform the hydrothermal sintering without inducing any phase transition (TiO2) or crystallization (SiO2) and without grain growth. The simplicity of the dissolution and precipitation reactions guarantees to exclude selective precipitation phenomena. We will show here how chemical and thermodynamical parameters can be tuned to enhance the mechano-chemical effects and improve the densification.

Keywords: Hydrothermal sintering, low temperature sintering, silica and anatase

38 - ABS 199

REACTIVE AIR BRAZING OF CERAMIC-STEEL COMPOSITES WITH MODIFIED SILVER-BASED PASTES

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Objectives Reactive air brazing of ceramics based on Ag-CuO type filler metals is a cost-effective way to produce ceramic-ceramic and ceramic-metal composites at air, without employing a protective gas atmosphere or vacuum. In addition to furnace technology, brazing by means of induction heating can also be used effectively. A considerable disadvantage of reactive air brazing is still the formation of pores or cavities in the brazing seams. The reasons for the emergence of theses pores or cavities has only partially been clarified so far. Besides an incomplete debinding of the brazing pastes, an insufficient wetting of the pastes as well as intrinsic side reactions of filler metals are discussed as possible origins of the defects.

Materials & Methods The sintering and wetting behavior of these reactive air brazing pastes were investigated by means of hot stage microscopy on various ceramic materials such as different grades of Al2O3, ZTA, and ZrO2. Joining tests were conducted on ceramic-steel composites by using a furnaces and an induction heated sample holder in order to permit short brazing cycles. The joint composites were analyzed utilizing non-destructive ultrasonic microscopy as well as scanning electron microscopy in order to investigate the microstructures in the brazing zones and interfaces.

Results Sintering investigations on different silver powder qualities revealed significant reboil effects at high temperatures, leading to an expansion of densified powder compacts, which are caused by evolving gases. Against this background, systematic variations of the brazing pastes concerning the copper type and content, the type of silver powder and binder components were scrutinized within this study. As a result, correlations between the filler metal composition, type of ceramic material, and brazing conditions were obtained.

Conclusions The formation of a pore-free brazing gap between the ceramic and steel is influenced by the morphology of the silver powder, the wetting of the paste at the melting range, and the debinding process during brazing at air. In combination with novel brazing pastes, the joining technologies at air reduce the processing costs for ceramic-steel composites.

Keywords: reactive air brazing, ceramic-metal composites

39 - ABS 26

SILICON CARBIDE MEMBRANES FOR REDUCED FOULING

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Fouling is challenge in all membrane applications and fouling control measures are a regular part of membrane operation. Fouling control methods range from simple backwashing to in-place-cleaning with strongly corrosive solutions or ozonation.(1) Together fouling and fouling control affects membrane lifetime, downtime and production rate(2) and thereby both construction costs and operation costs.(3)

Ceramic membranes have several advantages, with respect to polymeric membranes, with long life time, high flux and small footprint as some of the main characteristics.(4) Among the ceramic membranes, silicon carbide offers extreme stability under the chemically harsh conditions as experienced e.g. during chemical cleaning or during treatment of corrosive streams.(5)

It has been our ambition to develop an extremely smooth membrane to minimize fouling buildup on the membrane, using the most durable material maximizing membrane lifetime, even under chemically harsh conditions.

To this end we have studied the possible smoothness which could be obtained on a sintered Silicon Carbide membrane using different application techniques. This presentation will discuss the optimization of each technique and the optimal choice of technique for the case in question.

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Keywords: Reduced fouling, Membrane morfology, Chemical resistance

40 - ABS 935

NANOINDENTATION AND MICROSCRATCH TESTING OF BIOINSPIRED CERAMIC/CERAMIC COMPOSITES FROM BRITTLE CONSTITUENTS AS A FUNCTION OF THE PLATELET ORIENTATION: MECHANICAL RESPONSE AND CONTACT DAMAGE

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In ceramics, improving toughness usually relies on the introduction of a soft phase, mainly metallic or polymeric ductile phase, wich leads to a decrease on the mechanical behavior of the resulting material. Although natural materials that are both strong and tough succeed due to a combination of mechanisms operating at different scales, the relevant structures have been extremely difficult to replicate. Within this context, here we will investigate the micromechanical properties on a bioinspired approach based on widespread ceramic processing techniques for the fabrication of bulk ceramic/ceramic composite materials. Scarce number of studies have been reported, mainly focused on micromechanical properties as well as detailed analysis as a function of the lamella orientation by means of advanced characterization techniques.e.g. field emission scanning electron microscopy/focused ion beam (FESEM/FIB). A deeper knowledge is crucial to enhance the performance of these materials and to enhance their lifetime under severe working conditions.

In this study, a systematic nanomechanical study has been conducted in three different strong, tough and stiff bionspired ceramic samples from brittle constituents, each one with a different platelet orientation. The investigation included the use of range of indenter tip geometries to induce different stress fields and damage scenarios. Special attention has been paid to analyse main damage and fracture mechanisms as a function of the platelet orientation by FESEM/FIB.

It is found that the micromechanical properties (e.g. hardness and elastic modulus) determined at room temperature are not crucially affected by the platelet orientation, obtaining values around 30 GPa and 400 GPa of hardness and elastic modulus, respectively. No cracks are induced at the corners of the imprints performed by using a cube-corner indenter and, subsequently, the indentation fracture toughness is not possible to be determined. Within this context, the plasticity index is established in order to qualitatively estimate this parameter.

Finally, the scratch tests reveal several fracture mechanisms depending on the applied load, mainly Chevron cracks and spalling at low and high applied load.

Keywords: Bioinspired ceramic/ceramic, Nanoindentation, Scratch

41 - ABS 799

CHARACTERIZATION OF SiC IN Y_2O_3-STABILIZED ZrO_2 AS A CRACK SEALING AGENT IN THERMAL BARRIER COATING

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Nowadays the power costs and the environmental regulations are pushing to generate more efficient gas turbines, that means that must enhance the turbine inlet temperature.

Protective coatings are widely used to ensure a proper temperature isolation from the surface to the principal components. These pieces are exposed to temperatures higher than 1000°C, so a thermal barrier is needed. Ceramic materials are widely used as a thermal barrier coating (TBCs). The TBC is commonly composed of (a) metal substrate, (b) bond coat, (c) ceramic coat.

The Y2O3-stabilized ZrO2 (Y-TZP), is usually employed as thermal insulator in TBC, which allows to run gas turbines at high temperatures shunning the fusion of structural metals.

Nevertheless the high temperature exposition and the temperature changes on TBCs lead in cracks and delaminations which turns into a loss of properties. This kind of nuisance in TBCs due to thermal fatigue shorten its lifetime. To decrease this degeneration a self-healing material is produced. One of the frequently used materials is the SiC. The SiC can seal cracks due to an oxidation at high temperatures becoming a seal in cracks.

The aim of this work is to describe the self-healing behaviour of 15%Wt SiC in Y-TZP/Al2O3. The samples are base metal with a commercial Andry (NiCrCoAlY) interface and a Y-TZP/Al2O3 coat and metal/Amdry/Y-TZP/Al2O3+15%Wt SiC, these are plates with 100x10x2 mm the ceramic coat thickness between 165 and 185 μm obtained by Suspension Plasma Spray SPS.

The crack generation is developed by controlled mechanical deformation in a three point bending test.

The mechanical tests is done on a three point bending attachment in a universal testing machine Shimadzu. The gap between supports is 30 mm, the test were performed in three cycles. Each cycle is performed until reach approximately the 50% of the yielding stress of the base metal.

The thermal cycle to further the self-healing process is done at temperatures near 1000°C in one step for 30 minutes.

The crack sealing behavior is noticed:

- Mechanically by three point bending test with the aid of Acoustic Emission.
- Microstructurally by Optical inspection and a further FESEM examination with an EDS detector to get a map of the elements in and near the crack.

Keywords: Self-healing, Thermal barrier coatings, Acoustic Emission

42 - ABS 962

SUPPRESSING SPINODAL DECOMPOSITION BY INCORPORATION OF REDUCED GRAPHENE OXIDE INTO $(Sn_{0.5}Ti_{0.5})O_2$ SOLID SOLUTIONS

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The phase diagram for SnO2-TiO2 solid solution has the well-defined miscibility gap which is the phase-separation region including spinodal decomposition. The spinodally decomposed phases in SnO2-TiO2 system have been widely explored in fundamental phase transformation study as well as applications to gas sensors and photocatalysts, since it is one of few ceramic systems with spinodal decomposition. On the other hand, phase separation is sometimes regarded as an adverse phenomenon to be avoided in practical applications. In this presentation, we show that the incorporation of rGO into (Sn0.5Ti0.5)O2 solid solution suppresses its spinodal decomposition by structural characterization using X-ray diffraction (XRD) method and field-emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS). The mechanism will be discussed in terms of composition and oxidation state.

Keywords: (Sn,Ti)O2,Spinodal decomposition, Graphene

43 - ABS 691

MICRO-MECHANICAL TESTING OF THE BORON NITRIDE INTERLAYER IN SILICON CARBIDE/SILICON CARBIDE COMPOSITES FOR AERO-PROPULSION

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Ceramic Matrix Composites (CMC's) are finding renewed interest in the aerospace community for use as high temperature components in engines due to the potential for cooling air reductions over metallic parts, amongst other benefits such as weight saving and improving the turbine blade clearance. Quasi-brittle SiCf/SiC composites are toughened by the application of a boron nitride interphase coating to the fibre, which allows for cracks to deviate from the matrix. The principal issues faced by SiC-based composites lie in their degradation in corrosive environments (changing the interphase region and embrittling the overall composite) and their current inadequacy to adopt performance life models.

Maintaining the interfacial properties of the composite at high temperatures is therefore crucial. The extraction of these said properties has however proven itself to be a major engineering challenge in materials science. A few meso-scale and macro-scale techniques such as the transverse bend test and the Brazilian disc compression test have shown experimental reproducibility but are unsupported by sufficient modelling. The most accurate method for determining the properties at the micro-scale remains the push-out method on singular fibres.

Herein the poster will present current both advances in using the fibre push-out method and the challenges to overcome with the technique in order to accurately measure the interfacial shear stresses, coefficients of friction and residual compressive stresses at the fibre/matrix interface. Experimental data from the pushouts were fitted to common models to obtain more micro-mechanical properties. Statistics of pushouts with respect to indentation location (inter and intra-tow) have also been addressed. Quantitative results from fibre push-backs will also be highlighted. Finally, suggestions for improving the method to corroborate with ongoing modelling work will be showcased.

The poster features current ongoing challenges faced by the fibre pushout and pushback techniques and addresses potential solutions to fine-tune micromechanical properties of the interlayer in SiC/SiC composites with BN interlayers.

Keywords: Aerospace, SiC, BN, Fibre Pushout, Nanoindentation, Interfacial Shear Strength

44 - ABS 417

THE EFFECT OF CRYOLITE ON GRINDING OF STAINLESS STEEL

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The presented project focuses on the functional principle of cryolite as active filler in abrasive application. Despite its suitability, cryolite is considered hazardous to water and the environment which may result in a prohibition of use. Understanding the effect of cryolite on the grinding-efficiency is crucial to find surrogates. Active fillers are beneficial for the grinding process of hard-to-cut materials like stainless steels. Therefore, stainless steels offer a good chance to measure the effect of cryolite.

In this work simplified coated abrasives, consisting of a layer material, Al2O3 grains (Cerpass XTL in size # 60) and phenol resin, were used. The presented study compares coatings containing either Na3AlF6 (cryolite) or CaCO3 as reference. Grinding experiments were carried out with a pin-on-disk apparatus using a contact pressure of 85 kPa and an average grinding velocity of 38.7 m/s. Experiments were carried out with both abrasives and stainless steel (1.4301) pins. In further experiments pins with holes of 1.5 mm either filled with cryolite or left blank were heat treated at 850 °C in argon atmosphere for 18 h. After heat treatment the scale layer was removed on all surfaces before grinding. To quantify the amount of build-up-edges on the abrasive after grinding, dissolution experiments in HCl were carried out. The partially dissolved steel components were analyzed via ICP-OES. Cross-sections of the abrasives and the heat-treated pins were examined via SEM, EDX and TEM.

Despite its origin, cryolite in the system lowered the specific grinding energy: No major differences could be detected between cryolite-containing abrasives or heat-treated pins exposed to cryolite. This effect was accompanied by reduced amounts of build-up-edges on the abrasive, measured by ICP-OES. SEM, EDX and TEM measurements indicated reactions between cryolite and steel. A FexCr1-xF2 phase was found in the heat-treated pins, which were exposed to cryolite.

The effect of cryolite on grinding has not been completely discovered yet, nevertheless the interaction with steel is considered a major aspect. More specific, reduced amounts of build-up-edges seem to be an effect mechanism. Interactions between active fillers and the ceramic grains have not been found yet. However, further investigation of adhesion between build-up-edges and ceramic grains are planned.

Keywords: cryolite, abrasive, build-up-edge

45 - ABS 662

HIGH TEMPERATURE COMPRESSIVE BEHAVIOR OF DENSE Cr_2AlC AND Ti_3AlC_2 MAX PHASES OBTAINED BY SPS (REACTIVE) SINTERING

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Ternary layered compounds of transition metal carbides and nitrides, commonly known as MAX phase materials with the general formula of Mn+1AXn (M being an early transition metal, A being a group IIIA or IVA element, X being either C or N, and n=1-3) offer a unique combination of metal and ceramic properties. In the present work, the high temperature compressive behavior of dense compacts of Cr2AlC and Ti3AlC2 MAX phases has been assessed in the temperature range 800-1000 °C. In the case of Cr2AlC, the compacts were obtained by SPS sintering a high purity powder (CroMAX) for 5 min at 1200 °C under 50 MPa. In the case of Ti3AlC2, high purity dense compacts have been obtained by reaction SPS sintering for 15 min at 1325 °C under 15 MPa a TiC/Al/Ti powder mixture of molar composition 1:1,1:1. Prior to the mechanical characterization, the microstructure of the investigated compacts has been assessed by FIB-SEM-EBSD analysis. The typical microstructure of the Ti3AlC2 samples consisted of plate like grains with average size of 2-4 µm and length of 15-20 µm, that of Cr2AlC samples consisted of equiaxed grains with average size of 8-10 µm with traces of Cr7C3 and Al2O3. In both materials, only a slight degree of preferential crystallographic orientation was observed in the as sintered compacts resulting from the uniaxial loading in the SPS.

The assessment of the high temperature compressive behavior has been carried out by plasto-dilatometry. Cylindrical and parallelepiped samples were machined from SPS compacts by EDM. Samples were heated with a heating rate of 4°C/s by induction under vacuum. After stabilization, samples were deformed with a displacement rate of 0.01 mm/s up to various strain levels. The first results show that the flow stress of the material is significantly affected by the macroscopic deformation mode activated. On one hand, plastic deformation starts at very low flow stress under the occurrence of barreling, while on the other hand a high stress level is required when deformation occurs by shear banding. Finally, analysis of the damage level and mechanism in increasingly deformed samples were performed and discussed.

Acknowledgement

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Keywords: MAX phases, Compressive behaviour, Spark Plasma Sintering

46 - ABS 634

INFLUENCE OF POWDER PROCESSING ROUTE AND RARE EARTH ADDITIVES ON THE MECHANICAL PROPERTIES OF ZrB_2-SiC CERAMICS

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The influence of powder processing (various planetary milling conditions), and different content of Lu2O3, Yb2O3, Eu2O3 (2wt.%, 5wt.%, 10wt.%) on the sintering, microstructure evolution, phase composition, room temperature mechanical properties, thermal conductivity, oxidation and ablation resistance of ZrB2-SiC ceramics was investigated. All the samples were sintered at the temperature range of 2000-2050°C and the external pressure of 70-90MPa in Ar, using field assisted sintering technology. The relative density of the samples was always above 98%. A finer particle size and a higher amount of WC contamination in the powder did not lead to the better sinterability of the materials, while promoted the grain growth and the from β to α phase transformation of SiC. This led to the formation of plate-like SiC particles in the microstructure. On the other hand, when the powder processing route was optimized, the mixtures with the particle size around 1μm and the WC contamination below 1wt.% were obtained. This led to the higher density, finer microstructure, no from β to α SiC phase transformation, and the improved thermal conductivity and mechanical properties of the materials. The presence of different rare earth additives did not have a significant effect on the room temperature mechanical properties of the materials, but they all showed the improved properties when compared to the reference ZrB2-SiC materials without rare-earth additives. The effect of different rare-earth additives on the oxidation and ablation resistance was investigated by the static oxidation test and oxyacetylene torch, respectively.

Acknowledgment
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μμοσ

Keywords: zirconium diboride, ultra-high temperature ceramic, rare earth additives

47 - ABS 583

ELECTRODEPOSITION Ni-SiO_2 NANOCOMPOSITE COATINGS FROM AQUEOUS ELECTROLYTE CONTAINING SURFACTANT AND THEIR CORROSION BEHAVIORS

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containing two types of surfactant (sodium dodecyl sulfate,SDS,and cetyltrimethylammonium bromide, CTAB).The effect of surfactant on electrochemical process of Ni-SiO2 and the coating properties was investigated using cyclic voltammetry (CV), chronoamperometry (CA).The anticorrosion behavior of the coatings in 3.5 % medium were studied using electrochemical impedance Spectroscopy (EIS).The thin film coating was characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX),and x-ray diffraction (DRX).The experimental results show that the structure and the surface morphology of the coating depended of the types of the surfactants used.

Keywords: Composite, corrosion, steel,,electrodeposition,Ni-sio2 composite coatings

48 - ABS 571

TRIBOLOGICAL BEHAVIOR OF ZrB_2-30%SiC COMPOSITES AT ELEVATED TEMPERATURE

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Zirconium diboride (ZrB2 is one of the ultra-high temperature ceramics. It is expected to be used as tribo-parts in ultra-high temperature and oxidation atmosphere due to its good mechanical strength, oxidation-resistance, phase stablility, chemical stablility, and size stablility at high temperature. However, there are not sufficient studies about the tribological behavior of bulk ZrB2 and its composites. In this paper, the ZrB2-30 vol.% SiC composites were hot-pressed and the influence of tribopair, load, and temperature on the friction and wear properties of the composites were evaluated.

The results show that coupled with WC, under room temperature, at 0.1 m/s and 5 N, the average coefficient of friction (CoF) and specific wear rates (WRs) of the composites are about 0.72 and 4.47×10-4 mm3/N·m, respectively. While coupled with Al2O3, the CoF and WRs are about 0.76 and 9.47×10-4 mm3/N·m.

At room temperature and 0.1m/s, with the increasing of load, both the average CoF and WRs of the composites tend to decrease. At 10 N, the average CoF of the composites is as low as 0.58. At 20 N, the WRs is as low as 1.44×10-4 mm3/N·m. Besides tribopair and load, the CoF and WRs are affected strongly by temperature. Below and at 600 °C, the real-time curve of CoF-time is stable after running-in period; While at 800 °C, it fluctuates greatly. With the increasing of temperature, the average CoF and WRs tend to decrease firstly, and then increase. The average CoF is as low as 0.32 at 400 °C. The WRs is the lowest (2.45×10-4 mm3/N·m) at 600 °C, and is the highest (1.19×10-3 mm3/N·m) at 800 °C. Coupled with WC and Al2O3, the morphology of the worn surface shows different features at different stage and various types of tribolayers are formed on the worn surface. The wear mechanism is mainly mechanical wear.

Keywords: ZrB2-SiC,tribological behavior, high temperature

49 - ABS 479

CHARACTERIZATION AND OXIDATION BEHAVIOUR OF YB_4 AND ITS COMPOSITES

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Borides of rare earth metals are promising high-temperature materials with interesting chemical and structural properties. Considering the melting temperature and chemical stability, yttrium tetraboride (YB4) could be a suitable candidate for applications linked to extreme environments. As an additive, YB4 can act as a source of yttrium for the stabilization of zirconium oxide formed due to oxidation in a ZrB2 based Ultra High Temperature Ceramics (UHTCs). The oxidation behaviour of YB4, YB4-SiC and ZrB2-SiC-YB4 materials was studied under static and dynamic conditions up to a temperature of 2000°C. The phase composition of oxide scale formed during the oxidation process was determined by X-ray diffraction analysis (XRD). The degradation of materials was evaluated by the specific weight change after oxidation and the thickness measurement of the formed oxidized layer. Results showed that YBO3 was found as the main oxidation product of YB4 and YB4-SiC ceramics. Furthermore, SiC addition to YB4 matrix led also to the formation of Y2Si2O7 phase as a by-product of oxidation. Yttria stabilized zirconia was successfully formed during oxidation of ZrB2-SiC-YB4 above 1400°C. Moreover, selected physical properties of prepared materials were measured.

Keywords: ZrB2-SiC,YB4,oxidation

50 - ABS 339

USE OF $MoSi_2$ AS CRACK SEALING AGENT FOR ZIRCONIA MATRIX CERAMICS

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The technological development involves the creation of materials with better properties, capable of satisfying the needs for new applications. Yttria stabilized zirconia polycrystalline (YTZP) is widely used as a ceramic matrix material for structural applications due to its good properties, such as high oxidation resistance at high temperature, high elastic modulus, chemical corrosion resistance. Furthermore, mechanical properties as flexural strength and fracture toughness can be improved combining YTZP whit other materials.
Molybdenum disilicide (MoSi2) is used as matrix material for high temperature application due to its elevated melting point (2030 °C) besides it is also extensively used as a sealing agent. The use of MoSi2 as a reinforced agent for YTZP is not widely investigated.
The purpose of present investigation was to demonstrate the viability of MoSi2 reinforced YTZP matrix upgrading mechanical properties as much as achieving sealing functionality of composites at high temperature. YTZP/MoSi2 composites with different content of MoSi2 particles (from 5 wt% to 15 wt%) were obtained through colloidal processing, studying suspension stability to guarantee the homogeneity of composites, and subsequently sintered at 1500 °C by spark plasma sintering (SPS). This technique permits to control sintering energy, speed and provides larger reproducibility, therewith avoiding oxidation of MoSi2 during sintering leading to dense composites, which is indispensable to investigate the feasibility of MoSi2 as a sealing agent repairing cracks as long as they are being generated. When MoSi2 is exposed at high temperatures, under oxidation conditions, it is oxidized obtaining MoO3 gas and solid SiO2, which increases the volume thus filling the crack (and possible pores).
The composites had a relative densification of 95%, the hardness were similar to that of only YTZP obtained at the same conditions (~ 15 GPa) and toughness is improved when concentration of MoSi2 rises until values of 8.8 MPa/m1/2.

Keywords: ZrO2,Sealing,Spark plasma sintering

51 - ABS 337

EUTECTIC STRUCTURES IN QUASI-TERNARY ULTRAHIGH-TEMPERATURE SYSTEMS BASED ON ZrB_2 AND LaB_6

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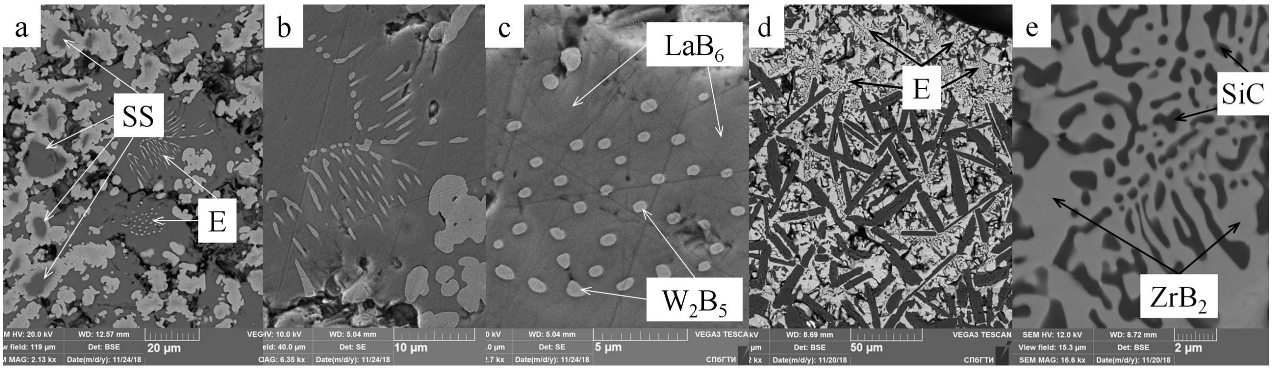
Phase equilibria in a large group of quasi-binary and quasi-ternary systems of refractory borides and carbides are described by eutectic phase diagrams. The main practical significance of eutectic systems based on ZrB2, HfB2, NbB2, TiB2, LaB6, W2B5, SiC and other refractory compounds is the dramatical decrease in the melting temperature of the eutectic system as compared to the melting points of the pure borides or carbides. This fact allows to activate pressureless sintering, hot pressing or SPS using rational choise of multicomponent systems to obtain composite materials with a high level of relative density (0.99-1).

In present work we investigated high-temperature interactions between components in two quasi-ternary systems: ZrB2-SiC-TaC and LaB6-W2B5-VB2. First of them is prospective for UHTCs applications, and second is one of the promising candidates for development of thermionic catodes and materials with special optical characteristics in near-infrared region. The aim of our study was: 1) to determine type of interactions (eutectic, solid solutions etc.) and 2) to measure eutectic teperatures and components concentration in eutectic region. Thermodynamic modeling of the liquidus surface in each system was carried out in accordance with the model of regular solutions. Calculated eutectic concentrations were used to prepare experimental samples.

Experimental samples were obtained via ceramic technology using commercial powders of LaB6, W2B5, VB2, ZrB2, TaC and SiC. Mixtures of powders were ball-milled using SiC balls, then pressed in the form of rectangular prisms 3x3x30 mm and pre-sintered at T = 2100 K and P = 0,01 Pa.

Melting of pre-sintered samples were performed using mini-furnace with graphite heater [1], equipped with a high-speed pyrometer. Fast cooling of the melted sample in Ar flow effectively fixed its structure for subsequent analysis. Crystallized objects were tested using XRD, SEM and EDX-analysis.

SEM-micrographs of crystallized samples are presented at fig. 1.



In both systems, the formation of a typically eutectic structure is observed (fig. 1 b, c, e). Non-equilibrium solid solutions formation are observed in the ZrB2-TaC-SiC system (fig 1 a). Different crystallite sizes indicate a strong influence of the temperature gradient in the cooling process on the growth of phase components. Experimentally determined eutectic temperatures are in good agreement with calculations: 2470 K (LaB6-W2B5-VB2) and 2670 K (ZrB2-SiC-TaC).

This work supported by RFBR (projects 18-33-20221 mol_a_ved and 18-53-18014 bolg_a).

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Keywords: eutectics, rare-earth borides, transient metals borides

52 - ABS 148

MORPHO-STRUCTURAL EFFECTS CAUSED BY ADVANCED CRYOGENIC GRADIENTS, OXIDATION AND THERMAL SHOCK ON EB-PVD THERMAL BARRIER COATINGS

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Thermal barrier coatings are advanced structural materials which have as a primary task to effectively protect the underlying substrate from hot corrosion and high-temperature oxidation. In this work we report the morpho-structural effects on TBCs upon cryogenic gradients, oxidation and thermal shock of EB-PVD coatings.
The substrates used in this study were refractory NIMONIC 80 alloy and izomolded graphite plates. The coating consists of three layers: NiCrAlY alloy as binding layer, ZrO2 substituted with 8 mol% rare earths mixtures and ZrB2. After 10h deposition time with a work pressure of 10-6 Torr, 10 kV work voltage, 260mA current intensity and 600°C temperature of the substrate the coatings were evaluated by means of XRD and FE-SEM which showed a good adherence and a continuous film along the substrate. The morphological characteristics refer to polycrystalline nature and polyhedral shaped granules with rounded edges with a mean size of 16,01 ± 6,19 μm.
Induced cryogenic gradients showed that the barrier coating with a thickness of 5-7 μm decreased the affected depth of the substrate from 15-17 μm to 5-7 μm. XRD and EDS analysis showed the formation of oxides Cr2O3 and Cr2NiO4 on the surface of the sample.
Thermal shock at 1200°C and oxidation at the same temperature for 5 hours resulted in the detachment of the coating and the oxidation of the substrate on a depth of 15 μm and, respectively, 30 μm.
Acknowledgment: Romanian Ministry for Research and Innovation, RDI Program for Space Technology and Advanced Research - STAR, project number 528 (Acronym Androtech)

Keywords: Microstructure, EB-PVD, Thermal Barrier Coating

53 - ABS 111

MICROSTRUCTURAL CHARACTERIZATION OF EB-PVD THERMAL BARRIER COATINGS

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The field of thermal barrier coatings (TBC) has greatly expanded in the last ten years, particularly in the phase composition and deposition technology. The search for this kind of materials is attributed to the increasing applications in the most demanding high-temperature environment of aircraft and industrial engines.

Two main processing technologies are generally used in the manufacture of TBCs, namely plasma spraying and electron beam physical vapor deposition (EB-PVD). In this work we report the microstructure characteristics of TBCs (stabilized ZrO2, ZrB2, ZrC, BaZrO3, La2Zr2O7) on different substrates (NIMONIC superalloy, niobium and graphite).

GI-XRD investigations proved obtaining the proposed phases but, in the case of binary oxide composition TBCs there is also present to some extent the decomposition of main phase. One way to improve composition stability of the TBCs was to deposit multiple layer with different compositions.

FE-SEM studies revealed that the processing parameters influence the continuity of the coatings and the growth microstructure. EDS mapping showed that the composition of the layers was homogenous and that there was no reaction at the interface between the substrate and the coating during processing or between the layers in the case of the composite TBCs.

Acknowledgment: Romanian Ministry for Research and Innovation, RDI Program for Space Technology and Advanced Research - STAR, project number 528 (Acronym Androtech).

Keywords: Microstructure, EB-PVD, Thermal Barrier Coating

54 - ABS 58

HIGH TEMPERATURE OXIDATION BEHAVIOUR OF (Hf-Ta-Zr-Nb)C HIGH ENTROPY CERAMICS

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Objective: High Entropy materials are associated with a “sluggish diffusion” effect, which is proposed to arise due to the chemical disorder introduced into the crystal lattice by the high entropy arrangement of multiple atomic species consisting of different atomic sizes and bonding preferences. It has already been reported that the reduced chemical diffusion of high entropy ceramics may offer advantages in terms of resistance to oxidation and corrosion [1-2].

The oxidation behavior of the high-entropy carbide (HEC) is an important consideration, given the thermally and chemically aggressive environments present in the typical target applications of these carbides. We report the oxidation behavior of the (Hf-Ta-Zr-Nb)C high entropy carbide (HEC-5), and a preliminarily investigation of the oxidation mechanisms.

Materials & Methods: The commercially available HfC (H.C.Starck, 99%), TaC (H.C.Starck, 99.5%), ZrC (American Elements, 99.5%), and NbC (American Elements, 99.5%) were used as the starting materials. The carbide powders were weighed in proportions and mixed by ball milling. The powder mixtures were sintered by Spark Plasma Sintering (SPS). A pure, single phase, high density (97%) HEC was obtained after sintering. The details of the materials processing can be found in our former work [3].

In order to study the oxidation behaviors of the HEC, thermogravimetric analysis combined with differential scanning calorimetry (TG–DSC) was performed from room temperature to 1300 °C. To further study the oxidation processes, oxidation testing bars were machined out of sintered HEC-5, and then heated at 800 - 1100 °C in a muffle furnace under air atmosphere. After the isothermal oxidation, the specimens were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray photoelectron spectra (XPS).

Results & Conclusions: In this work, single-phase, high density (97%) HEC consisting of transitional metals in equi-atomic amounts were synthesized using SPS. A TG–DSC investigation was carried out on (Hf-Ta-Zr-Nb)C samples in air in order to investigate their oxidation behavior. It was found that the HEC-5 displayed improved oxidation behavior in terms of its oxidation onset temperature, weight gain, CO2 gas production and the integrity of the oxidised particles, which expanded rather than disintegrated. Moreover, the influence of isothermal oxidation of (Hf-Ta-Zr-Nb)C on phase, composition and microstructure evolution were investigated.

Reference:
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[2] Shen, et al., J. Electrochem. Soc., 160, C531 (2013)
[3] Castle, et al., Sci. Rep., 8(1), 8609 (2018)

Keywords: High-entropy carbides, Oxidation behaviour, Microstructure

55 - ABS 38

INFLUENCE OF MACHINING ON BENDING STRENGTH OF Ti_2AlC AND Ti_3AlC_2 MAX PHASE CERAMICS

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The MAX phase ceramics represented by Mn+1AXn in general formula are layered ternary transition metal carbides and nitrides. The MAX phase ceramics has metal-like properties; electrical and thermal conductivities, good machinability possible to cut by any cemented carbide tool, high thermal shock resistance and high fracture toughness, and ceramic-like properties; low density and high Vickers hardness. In particular, Ti2AlC and Ti3AlC2, which are typical MAX phase ceramics, have good high-temperature oxidation resistance. These MAX phase ceramics are potential candidate to be used in various high-temperature applications. However, Ti2AlC and Ti3AlC2 may have a lot of surface cracks on the cut surface due to their brittleness after machining with a cemented carbide tool. This may lead to a remarkable decrease in mechanical strength of their MAX phase ceramics. Influences of cutting process on the mechanical strength of Ti2AlC and Ti3AlC2 MAX phase ceramics are investigated. Bending test was carried out for as-polished and as-milled samples. In this study, almost fully-densified Ti2AlC and Ti3AlC2 samples were prepared by the pulsed electric current sintering. X-ray diffraction revealed that no impurity phase exists in each sample. The values of bending strength were as high as 300 MPa in Ti3AlC2 and 500 MPa in Ti2AlC. Bending strengths of as–milled samples were comparable with as-polished ones. Surface finishing of the MAX phase ceramics by end milling with a cemented carbide tool does not give any significant influences for their bending strength.

Keywords: MAX phase ceramics, Bending strength, Machining

56 - ABS 17

PHASE CONSTITUTION, SOLID SOLUTION FORMATION AND PROPERTIES OF CARBON-DEFICIENT $Ta_{0.8}Hf_{0.2}C_y$ CERAMICS

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Objective: Ternary Ta0.8Hf0.2C ceramic has attracted the attention of researchers in recent years due to its ultra-high melting point (3905oC) [1], and outstanding mechanical and thermal properties. Owing to the same NaCl crystal structure (B1, space group Fm3m), Ta0.8Hf0.2C solid solution can be formed directly through TaC/HfC.

HfC maintains the cubic phase with a C/Hf ratio ranging from 0.56 to 1.0 while cubic TaC exists at a C/Ta ratio between 0.76 and 1.0. Based on early study by Storms [2], cubic TaC, rhombohedral Ta4C3, and the hexagonal Ta2C phases all exist over a range of stoichiometries relative to their nominal chemical formulae in the Ta-C diagram. However, carbon vacancies in the cubic solid solution carbide Ta0.8Hf0.2C phase have not been thoroughly understood.

It is well known that vacancies can directly affect the thermal and structural stability, and mechanical properties of materials. This work presents a preliminary study of carbon-deficient Ta0.8Hf0.2Cy (y=0.7, 0.8 0.9 and 1.0) ceramics of their phases, solid solution processing and thermo-mechanical properties.

Materials & Methods: TaC (Alfa Aesar, 99.9%), HfC (Alfa Aesar, 99.9%) and Ta (Alfa Aesar, 99.9%) were used as starting materials. The selected carbide powders were weighed in proportions, and mixed by ball milling at 200 rpm for 24 h in teflon pots, using SiC milling media, and stearic acid as a process control agent. The powder mixtures were sintered by Spark Plasma Sintering (SPS). A two-step heating profile with a 10 min pressureless degassing stage at 1800°C and a 10 min dwell at 2300°C was applied under a 40 MPa uniaxial pressure.

The bulk densities of the sintered samples were measured using the Archimedes' method with distilled water as the immersion fluid. Sintered samples were investigated by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

Results & Conclusions: Carbon-deficient Ta0.8Hf0.2Cy (y=0.7, 0.8 0.9 and 1.0) ceramics were densified up to 93.1 % from commercial powders via SPS at 2300°C. Carbon vacancies were introduced into solid solution lattice. The influence of different carbon vacancy concentration in Ta0.8Hf0.2Cy (y=0.7, 0.8 0.9 and 1.0) on lattice on the densification, microstructure evolution and solid solutioning process were investigated.

Reference:
[1] O. Cedillos-Barraza, D. Manara, K. Boboridis et al. Investigating the highest melting temperature materials: a laser melting study of the TaC-HfC system, Sci. Rep. 6 (2016) 37962.
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Keywords: Ta0.8Hf0.2C,Solid Solution, Carbon-deficient

57 - ABS 968

THE EFFECT OF SILICA ADDITION ON MECHANICAL PROPERTIES OF Ca-TZP

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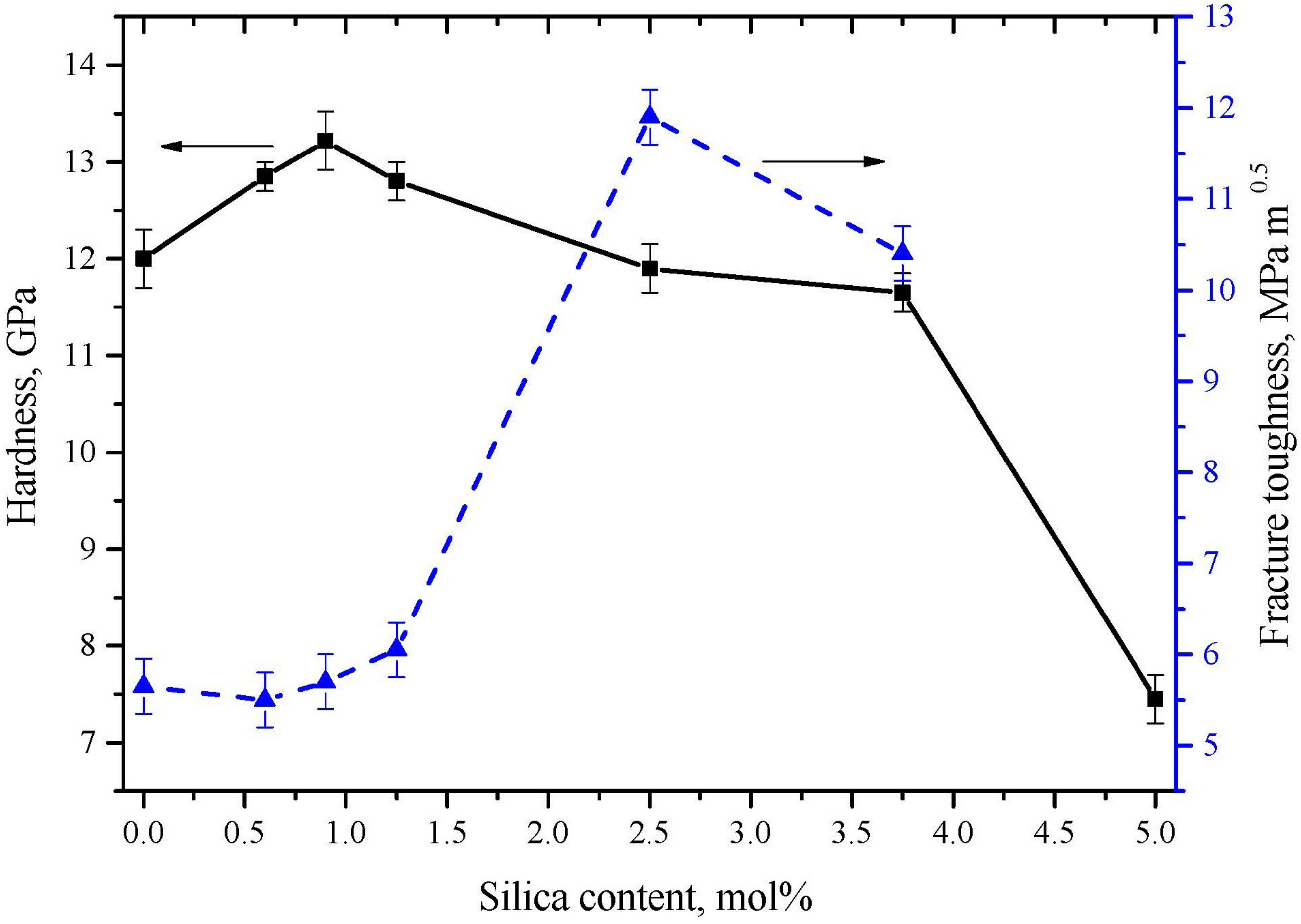
In the present study we have investigated the effect of silica addition on microstructure and mechanical properties of calcia-stabilized tetragonal zirconia polycrystal ceramic. The concentration of calcia was fixed â€“ 6.5 mol% as determined from our previous research. Silica content was varied in 0-5 mol% range. Addition of silica resulted in significant increase in fracture toughness of the material from 7.5 MPaâˆ™m0.5 at 0 % SiO2 to 12.5 MPaâˆ™m0.5 at 2.5 mol% SiO2 (figure 1). This change was also accompanied by minor growth of hardness from 12 GPa to 13 GPa. However, further doping with silica caused severe degradation of mechanical properties and destabilization of tetragonal phase resulting in spontaneous tetragonal to monoclinic transformation upon cooling at silica content above 3.75 mol%. Microstructural research suggested that silica when added to the material reacted with the calcia, lowering available amount of stabilizer, and thus enhancing transformability of tetragonal phase. The later indeed resulted in improved mechanical properties. According to scanning electron microscopy and energy dispersive X-ray spectroscopy assisted investigations silica-rich phases form glassy pockets at triple grain junctions and, presumably, a thin amorphous layer on the grain boundaries. The results allow us to consider silica as a useful dopant, capable of improving mechanical properties of calcia-stabilized zirconia.

Keywords: zirconia, silica, TZP



58 - ABS 710

Li-CONDUCTION ON NIOBIUM GARNET CERAMIC ELECTROLYTES FOR ALL-SOLID STATE BATTERIES

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Ceramic powders as solid electrolytes is promising to become the new generation of energy storage devices. They are safer compared with the conventional batteries, have ionic conductivity in the order of 0.0002 S/cm and also high electrochemical window (up to 5.5 V/Li), chemical and thermal stability, allowing its application in the most varied climatic environments. In this work, was performed the synthesis of Li-garnet based ceramic nanopowder by Spray Pyrolysis, that allows obtaining a two new Li5La3Nb2O12 and Li7La3Nb2O13 composition, containing nanograins in spherical shape. The dense electrolyte ceramic was obtained through the innovative Spark Plasma Sintering (SPS) technique that allows shorter sintering times at reduced sintering temperatures compared to conventional routes in which a pulsed direct current is applied in a graphite mold under uniaxial compaction pressure of 60 MPa. [1]

The Impedance Spectroscropy (Solartron SI 1260) was carried out in a range from 1 MHz to 0.01 Hz and by evaluation as a function of temperature it was possible to determine and differentiate the lithionic and electronic conductivities by Hebb-Wagner method.

The agglomerate size distribution was determined by Microtrac Analyzer that showed a powder with 95% has size less than 2.5 µm. Through Scanning Electron Microscope it was observed particles with diameter in nanometer scale (less than 100 nm). The X-ray diffraction allows identifies a powder with the LiLa2NbO6 pyrochlore phase and after the SPS occurs the transformation to the LLN-garnet crystalline structure with a lower temperature than conventional methods. [2]

After analyzing the preliminary conductivity results that were measured in a range of -10 to 100 °C (air atmosphere), the ceramic pellets synthesized in our research had indicated a lithionic conductivity up to 10-4 S.cm-1 and a charge transfer number of ~1, characterizing them as an inorganic solid electrolyte (ISE) with potential use as a device for high-energy storage applications.

Acknowledgments
The authors thank the financial support of this project by CBMM - Companhia Brasileira de Metalurgia e Mineração and EMBRAPII - Empresa Brasileira de Pesquisa e Inovação Industrial.

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Keywords: Electrolytes, Niobium, All-Solid State Batteries

59 - ABS 684

SYNTHESIS AND CHARACTERIZATION OF $Li_7La_3Zr_2O_{12}$ SOLID ELECTROLYTES WITH Yb ADDITION

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Nowadays, there is an undoubtedly need for renewable energy sources because of the petroleum-based energy source shortage. However, renewable energy sources such as wind and sun required being stored prior to use. Li-ion batteries are a well-known energy storage option because of high power and energy density, long cycle life and price. Their low thermal stability and toxicity are the main drawbacks that hinder widely usage of them. Such problems are mostly due to organic based liquid electrolytes in Li-ion batteries. In order to overcome these problems, oxide-based ceramic solid electrolytes are extensively studied until now. However, competitive performance is not observed because solid electrolytes have poor contact between electrodes and low ionic conductivity compared to liquid electrolytes. Garnet type Li7La3Zr2O12 (LLZO) based solid electrolytes have rather high ionic conductivity among other types of solid electrolytes and considered as a potential candidate for replacing liquid electrolytes. However, LLZO does not show a satisfying performance, yet. For that purpose, doping with various elements such as Al, Ga, Fe, Zn, Nb, Ta were investigated and a significant improvement on ionic conductivity is observed.

In this study, the effect of Yb addition in LLZO is studied. The atomic replacements between both La-Yb and Zr-Yb are also discussed. Yb is added up to 20 mole % per 1 mole of LLZO. The crystal structures of LLZO and possible impurity phases will be determined by XRD. The microstructure analysis will be conducted by using Scanning Electron Microscopy. The ionic conductivity of the sintered pellets will be calculated by using the AC impedance method.

Keywords: Li7La3Zr2O12,Solid Electrolytes, Li-ion Batteries

60 - ABS 429

NICKEL/OXIDE NANOCOMPOSITE CATALYSTS FOR METHANE REFORMING WITH CO_2

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Methane is known as a clean and renewable fossil fuel. Currently the most valuable way to utilize methane in industrial application is to reform it into syngas (a mixture of H2 and CO), which can be converted into liquid hydrocarbons through F-T reaction. Dry reforming of methane (DRM) consumes CO2, a type of global warming gases, hence it is beneficial to both energy and environment. The Energy-Environmental Materials Research Group at Shanghai Jiao Tong University developed facile hydrothermal methods to synthesize nickel/silica and nickel/alumina nanocomposites for efficient DRM catalysis. Both composite catalysts yielded high methane conversion ratio (above 80% at 750oC), mainly due to the finely dispersed Ni nanoparticles (particle size ~7 nm) on oxide supports with very high surface area. In addition, superior coke and sintering resistance in long term DRM catalysis is also observed compared to conventional nickel/oxide catalyst prepared by wet impregnation method. This is ascribed to the stronger metal-support interactions in the nanocomposite catalysts synthesized by hydrothermal methods followed with high temperature hydrogen reduction.

Keywords: CH4 reforming with CO2,nanocomposite catalysts, hydrothermal method

61 - ABS 522

MITIGATING STORAGE-INDUCED DEGRADATION OF Ni-RICH LAYERED CATHODE MATERIAL BY SURFACE MODIFICATION WITH A PROTECTIVE Li_3PO_4 NANOLAYER

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The Ni-rich LiNi0.8Co0.1Mn0.1O2 layered oxide (NCM811) is attracting considerable attention as a high-capacity cathode material for rechargeable Li-ion batteries. However, due to its inherent structural/chemical/electrochemical instability, NCM811 with high Ni content suffers from significant performance degradation upon storage even in ambient atmospheres as well as during charge–discharge cycling.
In this work, we demonstrate a simple but effective surface-tuning approach to mitigate storage-induced degradation of NCM811, which is based on the conversion of undesirable Li residues to a protective Li3PO4 nanolayer via phosphate treatment. An accelerated storage stability test (ASST) was performed under a controlled harsh environment to determine any storage-induced degradation of NCM811.
The ASST results provide clear evidence of degradation in the electrochemical performance of NCM811 upon storage: (i) the loss of initial discharge capacity, (ii) the accelerated capacity decay during cycling, and (iii) the evident potential shifts and area reductions of the redox peaks in the dQ/dV curves. However, the phosphate-modified NCM811 exhibits significantly reduced performance loss compared with that of the untreated one after being stored under harsh environmental conditions. The improved stability is attributed to phosphate treatment that eliminates Li residues inhibiting the formation of undesirable impurities and produces a thin Li3PO4 nanolayer mitigating the parasitic reaction between NCM811 and electrolyte. Furthermore, Li3PO4 serves as an effective protecting layer for H2O and CO2 infiltration during storage, thereby suppressing the deterioration of particle integrity.

Keywords: Ni-rich layered oxide, Lithium phosphate, Storage stability

62 - ABS 493

IONIC CONDUCTIVITIES IN GARNET THIN FILMS: STRAIN- AND PROCESSING-RELATED BEHAVIOR ANALYSIS

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All-Solid-State Batteries (ASSBs) are the important elements of the near-term future electrochemical energy technologies. Among all benefits one can pinpoint their safety, high energy density characteristics and openings for device miniaturization. One of the key elements of ASSBs are the solid electrolyte materials. Garnet-structured solid electrolytes can be seen as one of the most viable candidate material due to its chemical stability with Li metal anode, reasonable kinetic properties, transference number close to unit and wide electrochemical window [1, 2].

This study is focused on the analysis of the parameters affecting ionic conductivity in garnet LLZO and LLTO thin films. While studies of mechanisms responsible for ionic conductivity in the bulk attracts high attention there is surprisingly only limited number of studies on garnet films that have been published. In this study, the information on the parameters responsible for strain effects, defects and secondary phase formation (composition, method of deposition, elastic properties of substrate materials, thermal expansion characteristics, temperature processing and lattice mismatch) for the available published data have been used in our analysis and related with ionic transport characteristics. The relative contribution of considered parameters to ionic diffusion in garnet films have been unveiled, given observations were discussed and reinforced by additional literature analysis. The results obtained can be used to accelerate screening of new materials for Li ion ASSBs.

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Acknowledgements
Russian Foundation for Basic Research (RFBR project 17-03-00835) is gratefully acknowledged for support

Keywords: garnet-structured oxides, thin films, ionic conductivity

63 - ABS 446

BIPOLAR ALL-SOLID-STATE BATTERY WITH A PEROVSKITE-BASED BIPHASIC SOLID ELECTROLYTE

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The use of solid electrolytes provides a technical solution to address the safety issues of lithium-ion batteries and enables a bipolar design of high-voltage and high-energy battery modules. The bipolar design avoids unnecessary components and parts for packaging and electrical connection; therefore, it facilitates an increase in the volumetric energy density of the battery, while enabling easy build-up of total output voltage. Here, we design and construct a multi-layered, bipolar-type, all-solid-state battery (ASSB) using a biphasic solid electrolyte (BSE) based on inorganic Li0.29La0.57TiO3 perovskite and poly(ethylene oxide) (PEO). A flexible and freestanding BSE membrane exhibits high Li ion conductivity of ~0.12 mS/cm and shows enhanced electrochemical/thermal stability in comparison to a PEO-only solid electrolyte. A single-layer ASSB assembled with BSE shows promising electrochemical performance as evidenced by its high reversible capacity of ~123 mAh/g and excellent cycling stability over 100 cycles. Furthermore, a proof-of-concept bipolar ASSB comprising three unit cells connected in series is constructed using the BSE membrane and Al/Cu-cladded bipolar plates. The bipolar ASSB shows high thermal stability and operates reversibly without any internal short-circuit or current leakage during charge–discharge cycles, demonstrating that BSEs provide a promising approach to the design and fabrication of bipolar ASSBs with improved safety and high energy density.

Keywords: solid electrolyte, bipolar design, all-solid-state battery

64 - ABS 419

DEVELOPMENT OF DENSE CERAMICS ELECTROLYTES BASED ON $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ FOR APPLICATION IN SOLID STATE BATTERIES

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Nowadays, lithium batteries have the advantage of their weight and their energy storage capacity, being one of the best competitors in the market for electronic devices and electric vehicles. However, one of the main problems with rechargeable Li-ion batteries on the market is its electrolyte. Even with a high energy density, the actual batteries using liquid electrolyte have problems such as flammability, toxicity, low electrochemical stability, corrosion and possible of electrolyte leakage [1]. To solve these problems the solid electrolytes have been studied because they have low production costs combined with chemical stability, low environmental impact, high ionic conductivity and life cycle. Nanostructured ceramic materials are example as solid electrolytes,electrolytes and the $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLTO) stands out because its structure enables a significant increase in the Li-conductivity at 298K [2], thus making an excellent alternative for solid state electrolyte.

In this work, the reagents are calculated and weighed from the desired stoichiometry, dissolved in distilled water plus 20% ethanol v/v, and then their synthesis carried out via Spray Pyrolysis (SP) at temperatures of 800-950 °C, 4 L/min of compressed air as carrier gas and collected electrostatically by a high voltage source with 6.0kV. After collecting the ceramic powder, followed by morphological and structural characterization, it were founded peaks after analysis by X-Ray Diffraction (XRD) indicating the formation of La2LiTaO6 pyrochlore crystalline phase [3].

After the analysis, the powder was sintered via Sparking Plasma Sintering (SPS) at 800-1000 °C/, 50 MPa and 20 min. The analysis of the crystalline structure of the pellets was performed by XRD where it was observed that after sintering the pyrochlore phase with the cubic garnet single phase. The cubic garnet phase has the highest ionic conductivity, in the range of 10-5 S.cm-1 and 10-4 S.cm-1[6,7], measured by Frequency Response Analyzer (Solartron SI1260), with data collected in a frequency range from 1 MHz to 1 mHz and through of evaluation of resistivity as a function of temperature.

When synthesized via SP and the sintering via SPS is compared to the conventional means observed in the literature, we can observe a uniformity in the size of nanometric particles produced by SP and a better densification of the pellets, at lower time and temperatures, directly impacting the quality of the electrical result.

Acknowledgments
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Keywords: Spak Plasma Sintering, Solid State Electrolyte, Lithium-based Garnet

65 - ABS 260

Ga:In:ZnO PREPARED BY MAGNETRON SPUTTERING: INFLUENCES OF THE PREPARATION CONDITIONS ON OPTICAL AND ELECTRICAL PROPERTIES

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Transparent conductive oxides (TCOs) are a very important part in many optoelectronic devices such as solar cells and in new relevant devices for energy harvesting and storage such as photo-supercapacitors. Obtaining efficient solar cells and photo-supercapacitors requires a careful design of all of its parts. Transparent electrodes play an important role as an active part in the development of these devices An opportunity to obtain better TCO materials involves using ZnO compounds doped with Ga and In, that is indium–gallium–zinc oxide (GIZO). When properly doped, zinc atoms are substituted by trivalents atoms (X3+, where X = Al, In, and Ga).

C-axis textured thin films of gallium-doped indium zinc oxide (GIZO) with a 2% ratio of Ga/Zn, were obtained via RF-magnetron sputtering in co-sputtering mode on 1

and 2 cm2 glass substrates with high transparency and electrical conductivity. A Box- Behnken response surface design was used to evaluate the effects of the deposition parameters (In2O3 target power, deposition time, and substrate temperature) on the chemical composition, optical, electrical, and structural properties of the GIZO films.

The films were prepared in random order to include unidentified sources of variability in the experimental error. The crystalline parameters of the hexagonal structure changed with the In/Zn ratio and the charge carrier density was linked to those changes and therefore to the GIZO stoichiometry. The GIZO films grew c-axis oriented after an initial island step. The small percentage of Ga introduced early amorphization that led to an increase in the carrier mobility and conductivity. The increase in the solar absorptance due to the increase in the spectral absorptance in the NIR region was related to the plasma frequency and therefore to the charge carrier density. The charge carrier density and their mobility determine the conductivity. To obtain significant improvements, it is necessary to combine both adequately.

Figures of merit using weighted by functions for visible and solar, instead of the individual of the average values for the transmitted radiation or the absorption coefficient, were used to obtain an optimal compromise between transparence and conductivity. The best balance between conductivity and transparency for visible and solar applications of the GIZO films (2% Ga/Zn) as TCOs were in the In/Zn of 0.85-0.90 range.

Keywords: GIZO, Magnetron sputtering, electrical and optical propert

66 - ABS 164

CHARACTERIZATION ON MORPHOLOGY AND STRUCTURAL CHANGE BY CO-PRECIPITATION CONDITION OF Li[$Ni_{0.83}Co_{0.12}Mn_{0.05}$]$O_2$ CATHODE MATERIAL

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Li[Ni0.83Co0.12Mn0.05]O2 powders were synthesized from co-precipitated spherical metal hydroxide, (Ni0.83Co0.12Mn0.05)(OH)2. To determine the optimal metal solution concentration value, the CSTR co-precipitation was carried out at various concentration values (1.6 M, 2.4 M). The morphology of the synthesized precursor was observed by scanning electron microscopy. Calcination of the uniform metal oxide with LiOH at higher temperature led to a layer structured Li[Ni0.83Co0.12Mn0.05]O2, as a confirm X-ray diffraction. Also, the electrochemical properties and thermal stabilities of cathode materials were investigated using electrochemical testing and differential scanning calorimetry. Impedance test and cyclic voltammogram presented that internal resistance of the cell was dependent upon the concentration of metal solution. Such data is very helpful in determining the optimal content of metal solution concentration to enhancing electrochemical performance by adjusting powder size distribution and crystal structure.

Keywords: Metal solution concentration, Co-precipitation, Cathode material

67 - ABS 162

INTERESTING STRUCTURAL AND MAGNETIC FEATURES OF THE SHEAR STRUCTURE FeNb$_{11}$O$_{29}$

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FeNb11O29 is an intriguing and promising material that has been emerging in the last few years. [1] It is isostructural with Nb12O29, one of the rare compounds in which Nb displays a local magnetic moment and shows both antiferromagnetic ordering and metallic conductivity at low temperatures. [2] The main practical application of the iron niobate is in the field of lithium-ion batteries, as anodic material, for which a high structural stability is in general required. Both the two polymorphic forms of the FeNb11O29 have a shear structure consisting of edge- and corner-sharing octahedra with different distortion levels, in which the most suitable site for iron, at the centre of the structural blocks where regular octahedra were found, are determined. [3]
Whereas Nb12O29 has been widely studied, few magnetic data can be found on its analogous FeNb11O29, for which a role of the Fe3+ d electrons in affecting the magnetic behaviour can be foreseen. Another influence could be provided by the doping with transition metal cations that could at the same time improve the structural stability. In our work, we synthesized undoped FeNb11O29 and V-doped Fe0.8V0.2Nb11O29 samples. Both were then characterized from a structural and magnetic point of view. On the orthorhombic series of samples [4], also the electrochemical characterization in test cells vs metal lithium was performed. No antiferromagnetic ordering occurred up to 2 K, plausibly due to the lack of distinct conduction electrons that could help the localized spin interaction between neighbouring blocks. However, EPR and magnetic measurements disclosed the presence of Fe3+ in a high-spin configuration. [3]
The effects of doping are subtle for what concerns structural and magnetic features, but marked on the electrochemical behavior: where the undoped sample suffers from progressive capacity losses, the doped sample shows a great structural stability, offering stable and high performances.
Furthermore, the V-doped samples synthesized in Ar atmosphere showed interesting differences because crystallite size, cation valences and unit cell are influenced by the presence of Fe2+. The possible cause of the high structural stability can be inferred thanks to the structural study of this sample, that shows reduced distortion of the blocks producing a “zero strain” material, similarly to the most diffused Li4Ti5O12 anode.

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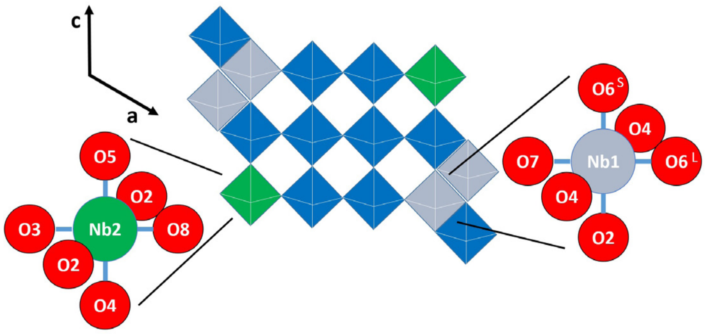
Keywords: Lithium-ion batteries,Diffraction,Shear structures



68 - ABS 71

SYNTHESIS AND CHARACTERIZATION OF ZEOLITE-TYPE CATALYSTS USED FOR PYROLYSIS OF VEGETAL WASTE

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Due to the high demand for energy worldwide and unreliable fossil fuel supply and prices, many research, and development efforts are focused on other sources of energy. Biofuels derived from lignocellulosic biomass, commonly known as second generation biofuels can overcome most of the limitations posed by first generation biofuel (ethanol and bio-diesel) derived from food sources. A wide variety of biomass in different parts of the world can be utilized for biofuel synthesis, including agricultural waste, organic residue, grassy and woody biomass along with dedicated biofuel crops.

Pyrolysis and gasification as well as the product upgrading can be performed by conventional heating or microwave heating, the latter being preferred lately due to its advantages, such as fast heating and start-up or short processing time. The resulting products from gasification and pyrolysis have certain limitations and cannot be used for application in their current state. Pyrolysis and gasification is accompanied using catalysts to improve the yields or quality of reaction products.

The main goal of our research was to study the synthesis and structural characterization of ZSM-5 zeolite type catalysts, as well as to simulate their potential behavior in pyrolysis and gasification process of different vegetal waste.

As starting raw material has been used ZSM-5 zeolite that was subjected to protonation to obtain HZSM-5 form of zeolite. Then, substitution of H from protonated form with different transitional metals (Me = Ni, Mo, Co, Fe2+, Fe3+) was employed. The purpose was to establish the catalytic ability of Me-ZSM-5 substituted zeolite during pyrolysis.

To establish composition and structural-morphological characteristics of Me-ZSM-5 catalysts there were performed X-ray analysis and Fourier Transformed Infrared (FTIR) spectroscopy before and after pyrolysis process. The results have shown the preservation of structural features even after use, confirming their good stability after calcination at 600 OC, the simulated temperature of pyrolysis. Morphological analyses have been done using Scanning Electron Microscopy (SEM) together with Energy Dispersive X-ray Analysis (EDAX) for elemental distribution and analysis.

The results were considered satisfactory and the first tests on both thermochemical and microwave assisted pyrolysis seem to be very promising.

Keywords: zeolite catalysts, pyrolysis, structure, morphology

69 - ABS 61

Sn/SiOCN NANOCOMPOSITE AS AN ANODE MATERIAL FOR THE LITHIUM ION BATTERIES

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Tin-based materials have been considered as promising anodes for lithium ion batteries (LIB) because of their high capacities. Sn-based materials can react with Li ions and form LixSny alloys such Li17Sn4 and Li22Sn5, which have theoretical capacity of and 959 and 994mAh/g, respectively, at room temperature[1]. Thus, the theoretical capacities of Sn based anodes are higher than that of graphite (LiC6, 372mAh/g) used in commercialized LIBs. However, large volume expansion and contraction during Li-uptake and release will cause the capacity fading and poor cycling life. Previous reports showed that surface modification of tin nanoparticles or introducing them into stable electronic/ionic conductor matrixes could suppress the degradation of their capacities [2]. On the other side, silicon-containing polymer derived ceramics (PDCs) have shown to be the promising candidates as anodes for lithium ion batteries because of their physical and chemical stability, high charge and discharge rates with gravimetric capacity [3, 4]. The lithiation capacity of PDCs anodes is due to the reversible Li-adsorption in the disordered carbon phase. However, PDCs anodes are poor electronic/ionic conductors. Anodes made from both Sn and PDCs materials are expected to show high capacity as well as good electrochemical properties. Therefore, in this report, we propose a one-step synthesis method to obtain tin-modified polysilazane precursor via the reaction of polysilazane with tin (II) complex and divinylbenzene (DVB). DVB has been chosen due to its high carbon content that required to increase the amount of free carbon in nanocomposites [5]. The synthesized precursors are pyrolyzed at 1100 Celsius in argon for 3h to obtain nanocomposite that consists of an amorphous SiOCN matrix and metallic Sn nanoparticles as revealed by XRD, XPS and TEM characterizations. The electrochemical performances of Sn/SiOCN nanocomposites show high a first cycle reversible capacity (800mAh/g) and stable cycling life due to the introduction of DVB and Sn nanoparticles that homogeneously dispersed in the stable amorphous ceramic matrix.

Keywords: polymer derived ceramics, nanocomposites, lithium ion anode materials

70 - ABS 951

HIGH CAPACITIVE NITROGEN-DOPED CARBONIZED MATERIAL DERIVED FROM PVP POLYMER

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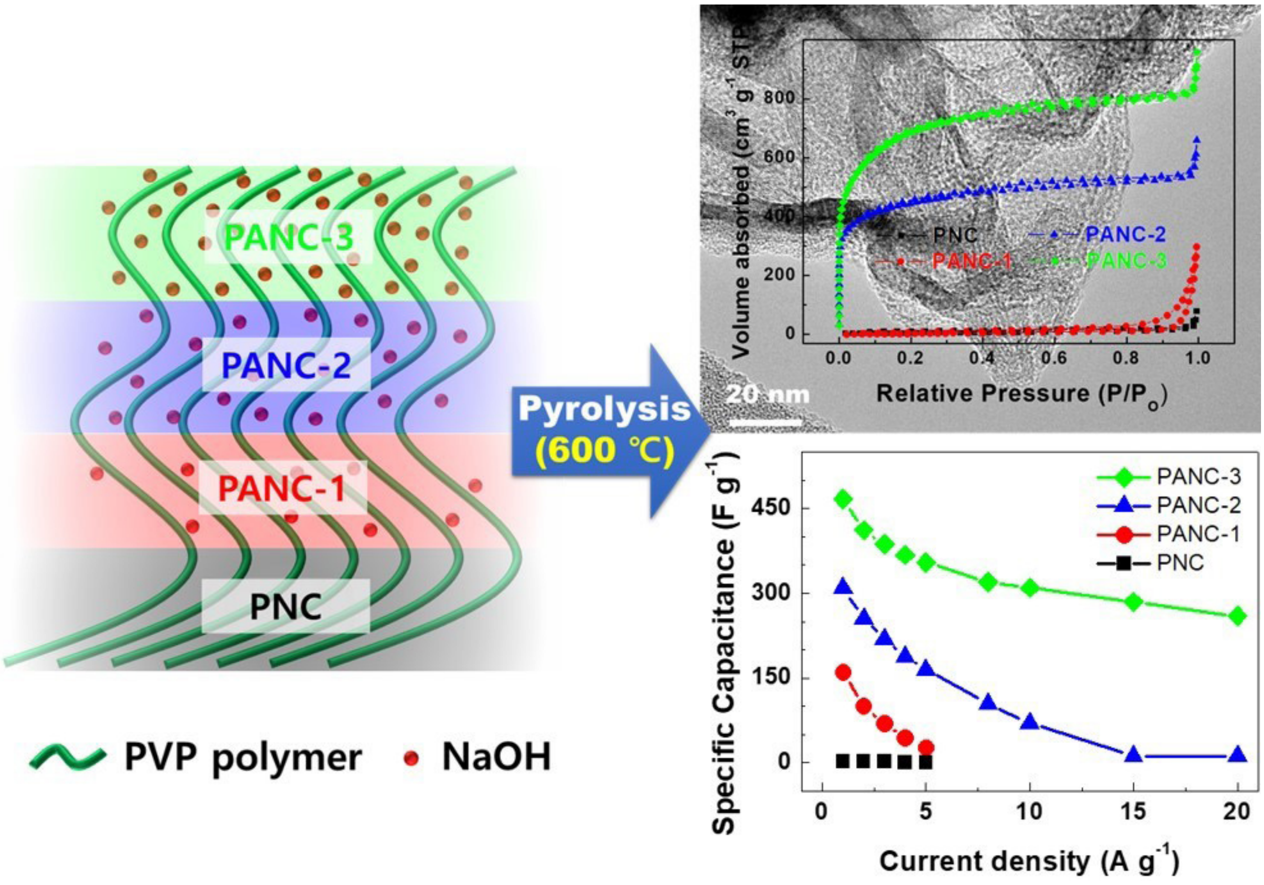
Supercapacitors (SCs) are an attractive device for upcoming energy storage systems because they can store higher energy than traditional capacitors and provide high power more expeditiously than batteries. Among electrode materials, carbon-based materials are one of representative basic research subjects as supercapacitive materials due to their low price, easy mass production, high electrical conductivity, excellent chemical durability and diversity of carbon composite materials. In recent years, in order to obtain the enhanced carbon-based electrode materials, the research of doping heteroatoms in a carbon framework for supercapacitive electrodes has drawn tremendous attention due to the highly active electrochemical performance characteristics of the resulting materials. Here, we present a method to synthesize highly porous nitrogen-doped carbon nanomaterials derived from a polyvinylpyrrolidone (PVP) material via a relatively low-temperature simultaneous activation/calcination process. As-obtained nitrogen-doped carbon materials characterize its chemical composition, morphology, specific surface area, etc. via XRD, FTIR, Raman, SEM, TEM, XPS, and BET equipment. Through these results, we suggest Furthermore, we demonstrate its excellent electrochemical properties by characterizing specific capacitance, cyclic stability, energy and power densities, etc.

Keywords: PVP polymer, Nitrogen-doped Carbon, High capacitance



71 - ABS 963

MN NANODOT-DISPERSED NI-Mn OXIDE NANOMATERIALS FOR HIGH-PERFORMANCE SUPERCAPACITORS

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Supercapacitors have attracted considerable interest over the past few decades owing to their fast charge and discharge rates, high power density, long cycle life, and high reliability. Herein, we developed a positive electrode composed of MnCO3 nanodots well decorated in and on nickel hydrogen carbonate–manganese carbonate hedgehog-like shell at needle (MnCO3 NDs/NiH–Mn–CO3) composites for high performance supercapacitor. The MnCO3 NDs/NiH–Mn–CO3 composite was directly grown onto a 3D macro-porous nickel foam as a binder-free supercapacitor electrode by a facile and scale-up hydrothermal method. The positive electrode exhibited a remarkable specific capacitance of 2641.3 F g-1 at 3 A g-1 and 1493.3 F g-1 at 15 A g-1. When fabricating an asymmetric supercapacitor using the MnCO3 NDs/NiH–Mn–CO3 as the positive electrode and graphene as the negative electrode, the device showed an energy density of 58.1 Wh kg-1 at a power density of 900 W kg-1 as well as excellent cycling stability with 91.3% retention after 10 000 cycles. The ultrahigh capacitive performance is attributed to the presence of the high surface area core–shell nanostructure, the well-dispersed and high conductivity of MnCO3 nanodots, as well as the synergistic effect between multiple transition metal ions. The superior supercapacitive performance of the MnCO3 NDs/NiH–Mn–CO3 makes them being promising positive electrode materials for high energy density asymmetric supercapacitors.

Keywords: Mn nanodot, Ni-Mn oxide nanocomposite, Supercapacitor

72 - ABS 10

PREPARATION OF <BETA>-ALUMINA CERAMICS WITH BOEHMITE NANORODS FOLLOWED BY FREEZE-DRYING

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Na-β-Al2O3 ceramic was prepared through boehmite nanorods followed by freeze-drying and solid-state reaction method. The relative content of β-Al2O3 phase, relative density, microstructure, and ion conductivity were characterized by X-ray diffraction, scanning electron microscopy, and AC impedance method. The results indicate that the relative density of samples are exceeding 95%, the relative content of β-Al2O3 phase are exceeding 96%. Using freeze-drying method, the samples have uniform microstructure, high densification and high conductivity.

Keywords: Na-beita-alumina, Ion conductivity, Freeze-drying

73 - ABS 879

CERAMIC PROCESSING AND MULTIFERROIC PROPERTIES OF THE PEROVSKITE $YMnO_3$–$BiFeO_3$ BINARY SYSTEM.

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Multiferroic magnetoelectric materials are interesting due to their prospective application in potentially disruptive technologies, such as electrically-tunable microwave magnetic components, spintronic devices or electrically-writable/magnetically-readable random access memories. However, only a few materials are both ferroelectric and ferromagnetic at room temperature, none of them with sufficient and robust magnetoelectric coupling.

One of the most promising approaches so far for obtaining multiferroic magnetoelectric materials are chemically engineered ABO3 perovskite oxides, in which multiferroicity is induced by introducing ferroelectrically and magnetically active cations in the A- and B-sites of the structure, respectively [1]. This is the case of BiFeO3, the most topical multiferroic material that shows multiferroicity at room temperature; and also of YMnO3, a geometric ferroelectric with a hexagonal structure. This latter compound presents a high-density metastable orthorhombic perovskite phase (o-YMnO3) that is multiferroic at very low temperatures. o-YMnO3 can be obtained by mechanosynthesis, as an environmentally-friendly and up-scalable alternative to high pressure synthesis [2].

We have recently succeeded in obtaining the whole perovskite binary system (1-x) YMnO3 – x BiFeO3 by mechanosynthesis. Phase evolution was studied, and a phase coexistence between polymorphs with orthorhombic (o-YMnO3) and rhombohedral (BiFeO3) symmetries was described in a range of compositions 0.6 =< x =< 0.9. This might be a promising polar-nonpolar morphotropic phase boundary (MPB), at which enhanced magnetoelectric properties can be obtained [3]. We report here the successful sintering of ceramics up to very high values of densification for selected BiFeO3-rich compositions, by using spark plasma sintering (SPS). This advanced technique allowed processing temperature and time to be significantly reduced, so that formation of secondary phases or perovskite decomposition were avoided. Ceramic microstructures were investigated with SEM, which confirmed high-densification, and revealed nanoscale grain sizes. The perovskite phase in ceramics was characterized by X-ray diffraction and Raman spectroscopy. Temperature dependent elastic and electrical measurements were carried out to investigate the evolution of the ferroelectric transition with decreasing x across the system, starting from BiFeO3 .Finally, magnetic properties are also presented.

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Keywords: Single-Phase,Perovskite-solid-solutions,Morphotropic-Phase-Boundaries

74 - ABS 972

THE EFFECTS OF S-DOPED rGO (SrGO) ON PHOTOCATALYTIC PERFORMANCE OF COPPER SELENIDE NANOSTRUCTURES

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Current research presents a comparison study about role of undoped reduced graphene oxide (rGO) and S-doped rGO (SrGO) on photocatalytic performance of copper selenide nanostructures under visible light illumination condition. The nanostructures were synthesized by a simple co-precipitation method under ambient conditions. Three types of the samples that were pristine copper selenide nanostructures with Cu3Se2 phase, Cu3Se2/rGO nanocomposites, and Cu3Se2/SrGO nanocomposites. Scanning and transmission electron microcopy (SEM and TEM) images showed that the Cu3Se2 nanostructures were decorated on two types rGO very well with different morphologies. X-ray photoelectron spectroscopy (XPS) and VU-visible (UV-vis) spectroscopy results indicated that valence band edge (VBE) and conduction band edge (CBE) positions of the samples were different. In addition, the Brunauer-Emmett-Teller (BET) results indicated that SrGO caused more porosity for the nanostructures. Photocatalytic experiments showed that, the photocatalytic performance of Cu3Se2 nanostructures was significantly improved by SrGO in compare with rGO. Electrical measurements indicated that, this improvement of the photocatalytic performance of Cu3Se2 nanostructures by SrGO was due to decreasing electrical resistivity of rGO by S-doping.

Keywords: Photocatalytic performance,Cu3Se2/SrGO nanocomposites, co-precipitation method, copper selenide nanostructures

75 - ABS 922

THE PHOTOLUMINESCENCE OF Eu:BaZr$_x$Ti$_{1-x}$O$_3$ CERAMICS

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The photoluminescence of BaZrxTi1-xO3 ceramics doped with 1 at.% Eu3+ at the Ba site was investigated as a function of composition (x = 0.0, 0.05, 0.15, 0.30, 0.50, 0.70 and 1.0) and temperature (-100 to 140°C). The ceramics were prepared by the conventional solid-state route and sintered at 1450-1600°C depending on composition. The low dopant concentration adopted guarantees that the structural and physical properties of the materials are not significantly affected. In particular, samples having x = 0.0, 0.05 and 0.15 show a typical ferroelectric behaviour while ceramics with x = 0.30, 0.50 and 0.70 are relaxors. BaZrO3 (x = 1) is a non-polar paraelectric solid. Irrespective of x, the ferroelectric ceramics show a rapid inversion of the intensity of the dominant 5D0 - 7F1 and 5D0 - 7F4 Eu3+ transitions at about 10 °C determined by the off-center displacement of Eu3+ from the dodecahedral Oh site of Ba2+ to a slightly distorted D4d site. The off-centering is attributed to cooperative polar interactions in the ferroelectric lattice, i.e. the correlated displacement of Eu3+ and Ti4+. The photoluminescence spectrum of the sample with x = 1 is dominated by the 5D0 - 7F1 transition in the whole temperature range, a clue that Eu3+ mainly occupies the Ba2+ centrosymmetric position. The ceramics with relaxor behavior show more complex photoluminescence spectra with an important contribution of the 5D0- 7F2 transition whereas the 5D0 - 7F4 line becomes strong only at progressively low temperatures with increasing x. The strong variation of the PL spectra induced by the temperature change can be exploited to develop ratiometric self-referencing luminescence thermometers.

Keywords: Polar order, Photoluminescence, Europium

76 - ABS 919

EFFECTS CAUSED BY THE ADDITION OF NIOBIUM PENTOXIDE ON THE ELECTROMAGNETIC PROPERTIES OF COBALT FERRITE.

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A comparative study of the structural and electromagnetic properties of cobalt ferrites, with and without niobium pentoxide addition, sintered at 1200°C and 1300°C was carried out. Niobium pentoxide was added to cobalt ferrite in order to increase its application in shielding systems and aerospace components such as radomes and RF and microwave sensors. Samples were prepared by the conventional method and the structural properties of the different compositions were evaluated by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) methods. The results showed the formation of a new phase in the samples containing niobium and allowed to observe the microstructural arrangements associated to the magnetic domains. The electromagnetic properties were evaluated by means of permittivity and permeability measurements obtained in the complex form by the NRW method (Nicolson-Ross-Weir) and the results used in simulation that allow us to visualize graphically the level of absorption of the electromagnetic wave associated to the material and its thickness.

Keywords: cobalt ferrite, niobium pentoxide, electromagnetic evaluation

77 - ABS 917

MICRO-, NANO- AND ATOMIC STRUCTURE INVESTIGATION OF ALKALINE NIOBATE BASED SOLID SOLUTIONS

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The market leading piezoelectric ceramics are, at the present moment, Pb(ZrxTi1-x)O3-based solid solutions. However, due to legislation and limitation of lead-based materials in commercial products [1], a big effort has-been put into study and development of more environmentally friendly alternatives.

Sodium potassium niobate (KNN) based materials have been proved to be valid substitutes of lead-based piezoelectric ceramics. Construction of phase boundaries by chemical modification was proved to increase the piezoelectric activity with respect to pure KNN [2-4]. One of the approaches includes formation of solid solutions of KNN-based formulations with alkaline-earth perovskites, such as CaZrO3 (CZ) [5-6]. Moreover, NaNbO3 (NN), one of the end-members of KNN solid solution, is a prototype lead-free antiferroelectric, however, trace impurities or low applied electric fields may induce ferroelectricity. It has been shown that forming solid solutions of NN with CZ can be a strategy to stabilize the antiferroelectricity [7]. Such materials could then be used in energy storage.

In the present study, we primarily focus on the microstructure, domain configuration and domain structure of selected alkaline niobate based solid solutions. Both Li, Ta and Mn-doped KNN-based solid solution with CZ, as a representative lead-free piezoceramic, and NN-CZ solid solution as a lead-free antiferroelectric are considered.

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Keywords: Alkali-niobates,Microstructure,Domain structure

78 - ABS 716

PHASE STRUCTURE, DIELECTRIC, RAMAN AND PIEZORESPONSE INVESTIGATIONS IN SOL-GEL DERIVED BCZT CERAMIC

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Objective $(Ba_{0.85}Ca_{0.15})(Zr_{0.10}Ti_{0.90})O_3$ (BCT-BZT) bulk ceramics of the morphotropic phase boundary (MPB) composition were synthesised by the cost-effective sol-gel process. Structural studies were performed using in-situ X-ray diffraction and SEM/EDS methods. Exhaustive temperature dependent Raman and dielectric measurements were undertaken to elucidate the phase transition behaviour that suggested the presence of three phase transitions in the studied ceramics.

Materials & Methods Synthesis of powder by sol-gel synthesis route based on the complexation of alkoxides by acetic acid was accomplished using analytical grade chemicals. Phase formation of the sintered samples (hereinafter referred as sg-BCZT) was established using XRD in the range 20-80°. Surface morphology and the elemental distribution mapping were obtained on the as-sintered surface. Raman spectra and dielectric properties were measured as a function of temperature. Piezoresponse Force Microscopy (PFM) experiments were performed using a commercial atomic force microscope (NT-MDT).

Results Refinement analysis revealed a coexistence of tetragonal, T (space group P4mm) and orthorhombic, O (space group Amm2) symmetries in sg-BCZT. The refined lattice parameters for the tetragonal phase are a=b=3.9985(1) Å and c=4.0076(4) Å with unit cell volume of 64.073 Å^3.
Microstructure of the as-sintered surface of sg-BCZT revealed a grain morphology consisting of few isolated intergranular pores with grains of an estimated average size ~2.41±0.71 μm.
Elemental distribution mapping suggested a homogenous distribution of all the constituent elements (Ba, Ca, Zr, Ti, O).
Detailed analysis of dielectric and Raman results, signal anomalies at: -50±5 °C, 40±5 °C and 120±10 °C, signifying the existence of three phase transitions namely: <FILE IMAGE='70_20181214082323.jpg'>. Additionally, analysis of loss data revealed a relaxation phenomenon in the region close to -100 °C, attributed to the viscous/hysteretic motion of the domain walls.

Conclusions Rietveld analysis of XRD data ascertained coexistence of ferroelectric tetragonal and orthorhombic symmetries in the sg-BCZT sample. A microstructure with few scattered pores was obtained with grains of average size 2.5 μm. Homogeneous elemental distribution at global scale was observed by EDS. Crystallographic transformation temperatures estimated from the loss of intensity for several phonon modes in the temperature evolution of Raman spectra, agreed well with that obtained by the dielectric method. Piezoresponse measurements revealed a typical domain configuration as exhibited by the parent BTO. The phase sequence in sg-BCZT was concluded as:

Keywords: Lead-free ceramics; sol-gel

79 - ABS 912

DOMAIN STRUCTURE OF FINE- AND COARSE-GRAINED BARIUM TITANATE CERAMICS: EFFECT ON THE MACROSCOPIC RESPONSE

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Polycrystalline barium titanate, BaTiO3 (BTO), is one of the most studied ferroelectric ceramics. Consequently, it is well established that BTO macroscopic properties are directly linked with the grain size, which plays a key role in arranging the domain structure. In this work, a direct correlation between domain structure and macroscopic properties of BTO ceramics is evidenced. Fine- and coarse-grained BTO ceramics are obtained by conventional solid-state processing. The domain structure of the obtained ceramics is revealed by confocal Raman spectroscopy. Results show that only 180° domain walls appear in fine-grained ceramics while 90° domain walls are shown in coarse-grained ceramics. Macroscopic dielectric, ferroelectric and piezoelectric responses correlate with domain structure. Fine-grained BTO exhibits poor dielectric and ferroelectric response compared to the coarse-grained BTO performance. Furthermore, a negligible electric-field-induced strain is shown in fine-grained BTO as a result of the absence of ferroelastic (non-180°) domain walls. Intrinsic and extrinsic contributions are evaluated through the temperature dependence of macroscopic properties. Results confirm that extrinsic (domain wall) contribution determine the macroscopic response of BTO ceramics, as expected.

Keywords: domain structure, barium titanate, grain-size effect

80 - ABS 535

TRUE-RAMANENT POLARIZATION AND RESISTIVE LEAKAGE ANALYSES IN HIGH PERFORMANCE PIEZO-/PYROELECTRIC Ho-DOPED 0.64Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.36PbTiO$_3$ CERAMIC

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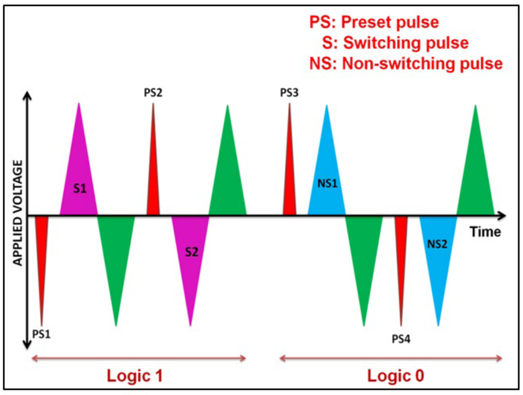
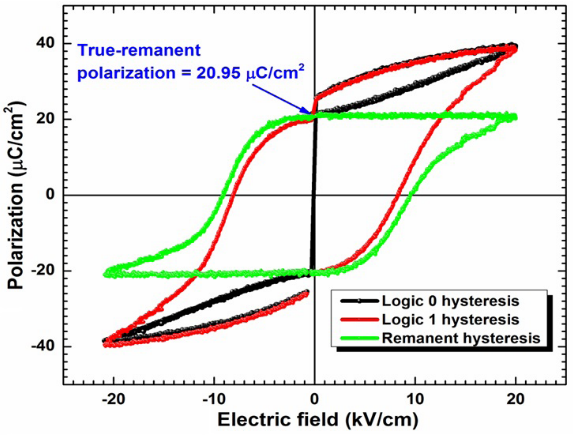
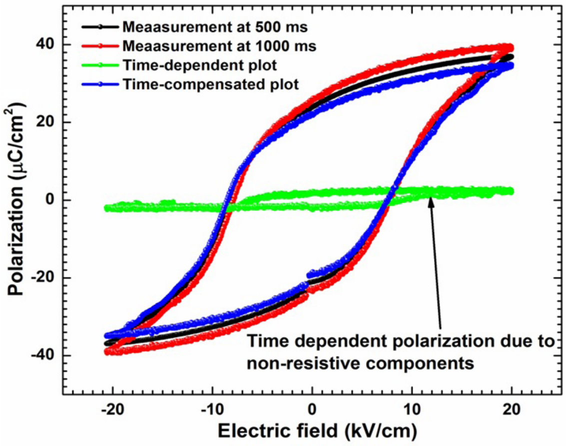
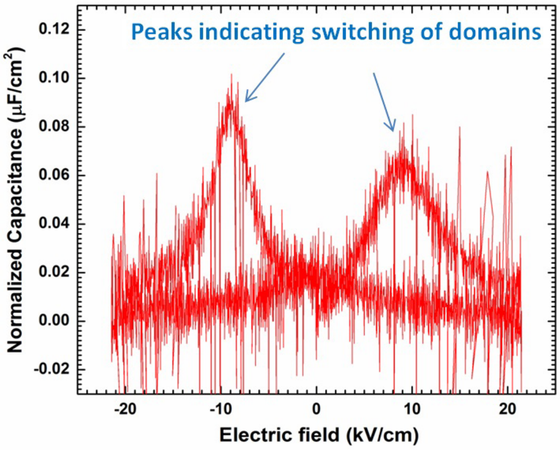
In this work, the ferroelectric properties of holmium doped 0.64Pb(Mg1/3Nb2/3)O3-0.36PbTiO3 (Ho-doped PMN-PT) ceramic including determination of intrinsic polarization and investigation of resistive leakage was presented in detail. The effect of Ho3+ doping on the structure, dielectric, piezoelectric and ferroelectric properties of PMN-PT ceramics was studied. Perovskite phase of pure and Ho-doped 0.64Pb(Mg1/3Nb2/3)O3-0.36PbTiO3 ceramics were synthesized using solid state reaction method. Powder XRD and EDX analyses confirmed the incorporation of Ho3+ ions in the PMN-PT lattice. The average grain size, transition temperature and dielectric loss factor decreased while the density and the dielectric constant of the PMN-PT ceramic increased by Ho doping. Furthermore, an increase in the ferroelectric properties (spontaneous and remanent polarizations) and the piezoelectric coefficient (d33*, from 547 to 610 pm/V) were observed for doped sample. The 'Remanent Hysteresis Task' revealed that a major portion (80.42 %) of the remanent polarization (Pr) is switchable in the sample which makes Ho-doped PMN-PT a potential material for memory switching devices applications. Time-dependent compensated (TDC) hysteresis task and fatigue test were carried out which revealed resistive leakage and fatigue free nature of Ho-doped PMN-PT ceramic. These results demonstrate that the Ho-doped PMN-PT ceramic possesses excellent properties to achieve a variety of applications.

Keywords: Piezoelectric property, Pyroelectric property, True-remanent polarization









81 - ABS 898

ENHANCED PIEZOELECTRIC PROPERTIES OF K/Na EXCESSED (Na,K)NbO$_3$-BiScO$_3$ CERAMICS WITH TWO-STEP SINTERING PROCESS

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Lead-based piezoelectric ceramics have been widely employed in electronic device applications such as sensors, actuators and resonators due to their excellent piezoelectric properties. However, the toxicity of lead in Pb(Zr,Ti)O3 (PZT) can contaminate the environment and damage human health. Therefore, lead-free piezoelectric ceramics with high piezoelectric properties have been researched to replace lead-based piezoelectric ceramics. As a representative lead-free ceramic, Na0.5K0.5NbO3 (NKN) ceramic has been considered a candidate for lead-free ceramics because of its superior piezoelectric coefficient of 88 pC/N and high Curie temperature of 420 °C. However, dense NKN ceramics are difficult to be obtained because of the volatilization of potassium and sodium at high sintering temperature. To complement this drawback of NKN ceramics, many processing technologies have been developed and extensively studied. In this research, the K/Na excessed (1-x)Na0.5K0.5NbO3-xBiScO3 (NKN-BS) ceramics were prepared by employing two step sintering method.

As adding Na and K to NKN ceramic, we expected that electric and piezoelectric properties improved because of compensate for volatilization of sodium and potassium. Also, BiScO3 has been study to excellent material with large dielectric and piezoelectric properties. The K/Na excessed NKN-BS ceramics were researched by varying the sintering temperature in order to optimize its piezoelectric properties. Also, the effects of dwell time for the two step sintering process on the ceramic properties were studied.

Keywords: lead-free ceramic, two-step sintering process, K/Na excessed NKN ceramic

82 - ABS 893

OPTIMUM PIEZOELECTRIC ENERGY HARVESTER BY IMPEDANCE MATCHING

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In these days, we have faced the problems of energy depletion and environmental pollution as increasing industrial facilities. Many researchers believe that these environmental energy crises can be solved by introducing the sustainable clean energy support from the renewable energy sources such as piezoelectric energy, thermoelectric energy, wind energy and solar energy. [1] To use the piezoelectric energy, piezoelectric materials with high efficiency should be considered. In these days, many lead free piezoelectric materials and devices were proposed to use actuators, sensors, and energy harvesters. However, the lead free piezoelectric materials have limits for the applications due to their low piezoelectric efficiency. Therefore, there are still strong demand to use lead based materials with decreased content. Among these materials, BiScO3-PbTiO3 (BS-PT), perovskite structured BiMeO3-PbTiO3 piezoelectric energy harvester attracts attention because of its high Curie Temperature. Especially, the composition ratio of 0.36BS-0.64PT was shown the highest piezoelectric, dielectric properties and Curie Temperature. [2] As other BiMeO3-PbTiO3 based materials, both of Bi(Ni1/2Zr1/2)O3-PbTiO3(BNZ-PT), and Bi(Mg1/2Zr1/2)O3-PbTiO3(BMZ-PT) can be the emerging materials for the piezoelectric device applications. These materials can be the promising piezoelectric materials not only can reduce the ratio of lead, but also enhance dielectric properties than BS-PT. The piezoelectric properties of BNZ-PT and BMZ-PT are competitive in comparison with BS-PT and dielectric property of that is higher than BS-PT. In general, the generated piezoelectric energy can be stored in the capacitor or battery. However, to store the energy in the large sized capacitors or batteries, impedance between the input and output system should be considered, otherwise energy cannot be stored and then reflected. Therefore, in this paper, the required conditions to generate and store the maximum energy through impedance matching technique. To introduce the impedance matching technique, simulation tools of Pspice will be introduced and discussed.

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Keywords: Energy Harvesters, Impedance

83 - ABS 890

INFLUENCE OF IMPURITIES AND THE STOICHIOMETRY ON THE PIEZOELECTRIC PROPERTIES OF BARIUM TITANATE

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Piezoelectric materials are part of our daily routine: whether as microelectronics, sensors or actuators. One of the most used piezoceramics is lead zirconate titanate. However, due to the toxicity of lead, its use is becoming increasingly restricted and the search for materials with similar or better properties is of great economic, environmental and social interest. Barium titanate is a classic functional ceramic and is widely used in systems designed to replace materials with toxic content. In this work, a thorough investigation was carried out on the influence of impurities from the raw material and the Ba/Ti ratio on the piezoelectric response of barium titanate. Samples with different amounts of impurities and Ba/Ti ratios were prepared. The samples were characterized by X-ray diffraction, Scanning Electron Microscopy, and piezoelectric measurement. As the degree of impurities increased, there was a considerable increase in the number of intragranular pores and an attenuation in the piezoelectric response. However, there is no strong influence on grain growth and the polarization curve. The Ba/Ti ratio, in turn, exerts a considerable influence on grain growth and deformation curve. Samples rich in Ti tend to form much smaller grains relative to samples with barium content. At the same time, the material rich in Ba has a negative strain, an effect that is not observed in the samples rich in titanium.

Keywords: Barium Titanate, Piezoelectric, Impurity

84 - ABS 886

EFFECTS OF Li DOPING ON THE DENSIFICATION AND PIEZOELECTRIC PROPERTIES OF BCZT CERAMICS

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$Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCZT) ceramics have been investigated as a promising lead-free ferroelectric ceramic with an extremely high d_{33} value of ~600 pC/N. The giant piezoelectricity of BCZT mainly stems from the T-O phase boundary due to easier polarization rotation and larger lattice softening. However, one of the barriers preventing it being widely used in the near future is its high sintering temperature. Li_2CO_3, as a sintering additive of low valence, has been widely used in BZT and BCT systems to lower the sintering temperature and improve the densification and electrical properties of ceramics, but its high volatility causes problems during sintering. In this work, Li_2CO_3 was added to the calcined and ball-milled BCZT powder to promote the formation of liquid phase during sintering. BCZT + x mol% Li (x = 0 ~ 0.2) ceramics were prepared using the solid-state reaction method. The effects of Li_2CO_3 content on the microstructure and piezoelectric properties of BCTZ ceramics is investigated, and the underlying physical mechanisms are clarified.

Keywords: Piezoelectric ceramics, BCZT, Li doping

85 - ABS 878

SUBSTITUTION OF ZIRCONIUM IN LEAD-LANTHANUM-ZIRCONATE-TITANATE BY HAFNIUM

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The influence of hafnium substituting zirconium in lead lanthanum zirconate titanate (PLZT) on the antiferroelectric properties is investigated. PLZT may be used for multilayer ceramic capacitors, which fit high DC voltage applications in power electronic systems and offer high charge density at moderate field stress due to anti-ferroelectric characteristic.

Hafnium as substituent for Zirconium offers the opportunity to investigate the influence of atomic mass on dielectric properties, because charge and atomic radii of Hf^{4+} and Zr^{4+} are the same. Samples of $Pb_{0.91}La_{0.06}(Hf_xZr_{1-x})_yTi_{1-y}$ (x:0 to 0.3; y: 0.9 or 0.85) were prepared using mixed oxide method, calcinated at 850°C and sintered at 1250°C. The incorporation of hafnium into the material was controlled using X-ray powder diffraction and scanning electron microscopy.

Since in previous studies the influence of this substitution on switching field and polarization was found to be neglectable, special attention was paid to phase transition temperatures of this system. Therefore dielectric permittivity versus temperature as well as differential scanning calorimetry was measured to determine phase transition temperatures.

The data obtained show that the variation of atomic mass has minor influence on phase transition temperatures of the AFE-FE phase transitions and cause only a slight increase of FE-PE phase transitions.

Keywords: PLZT, Isovalent substitution, Hafnium doping

86 - ABS 948

BILAYERED AND MULTI-LAYERED MULTIFERROIC OXIDE THIN FILMS FOR APPLICATION IN ULTRAFAST OPTO-MAGNETO-ELECTRONICS

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Recent applications of multiferroic thin films in ultrafast opto-magneto-electronics and memristors opened broad range of new opportunities in this field. Thin films offer new functionality in materials, since their physical parameters can be mediated by the strain at the interface. This strain can directly couple ferroelectric and ferromagnetic orders, producing strong magnetoelectric coupling influencing much lower power consumption, high speed processes, and greater electric/magnetic field controllability. The coupling between electric and magnetic order, especially optically imposed on ultrafast timescales is one of the priority directions nowdays. However, it is important to design appropriate structures, such as multiferroic layered composites in which the magnetoelectric coupling can be engineered through proper choice of the interface geometry and constituent phases.

Here we present different bilayered and multilayered structures, composed of feroelectric doped-BaTiO3 and magnetic doped-LaMnO3 and NiFe2O4 layers, obtained by solution deposition and chemical vapor deposition techniques. The obtained thin films (having layer thicknesses up to 50 nm) were structurally characterized by XRD, TEM and Raman spectroscopy. Well-defined layered structures were confirmed, together with a capability to design desirable crystalline nature of the fabricated multiferroic thin films. Dielectric, ferroelectric and magnetic properties were also investigated and compared with already published data.

Keywords: thin films, multiferroics, oxides

87 - ABS 869

COMPOSITION-DEPENDENT CHARACTERISTICS OF Ce^{3+}-DOPED $BaTiO_3$ CERAMICS DERIVED FROM SOL-GEL POWDERS AND SINTERED BY ALTERNATIVE TECHNIQUES

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Pure and cerium-doped barium titanate nanopowders described by the formula Ba1-xCexTiO3 and Ba1-xCexTi1-x/4O3 for (x = 0.05) were prepared by the sol-gel method, using barium acetate, cerium nitrate and titanium isopropoxide as precursors.
After annealing at 900oC for 2 hours, the non-stoichiometric powders with built-in Ti vacancies (Ba1-xCexTi1-x/4O3) show single phase compositions for both samples while the stoichiometric powders described by the formula Ba1-xCexTiO3 show small amounts of secondary phases (Ba2TiO4 and BaTi2O5). TEM investigations of the powders with built-in Ti vacancies show an average particle size of 62 nm for the sample with x = 0.005 and 50 nm for the ceramic with x = 0.05. SEM investigations of the ceramics sintered at 1300oC for 4 hours indicate significant changes of the microstructural features as a function of dopant content and stoichiometry. More homogeneous and denser microstructures were observed for the ceramics with built-in titanium vacancies than in the case of the ceramics free of compensating defects. The ceramics obtained by spark plasma sintering exhibit denser microstructures and lower average grain size, relative to the samples with similar composition resulted after conventional sintering. Relative density values of 98.5 % and average grain size values of 0.1 μm, were determined for the ceramics with x=0.05. The microstructure exhibits a pore-free specimen with unimodal grain size distribution, a higher densification and consists of small, equiaxial grains, with well-defined boundaries and perfect triple junctions. FE-SEM investigations in BSE mode did not reveal the presence of the secondary phases detected by XRD measurements, most likely, because of their small amounts. The ceramic exhibits acceptable low dielectric losses (tan δ~ 0.01).
A sharp ferroelectric-paraelectric transition is obtained for all the ceramics but the values of the Curie temperatures (TC) are very different. TC is close to room temperature (TC = 24°C for Ba0.95Ce0.05TiO3, TC = 21°C for Ba0.95Ce0.05Ti0.9875O3). Due to the proximity of the paraelectric – ferroelectric phase transition, the ceramics present at room temperature higher dielectric permittivity values (εr = 5904, for the stoichiometric sample and εr = 7698, for the sample with built-in Ti vacancies).
The spark plasma sintered Ce-BaTiO3 specimen shows a fine-grained microstructure and an almost temperature-independent colossal dielectric constant (~ 3.35 ~ 106).

Keywords: BaTiO3,sol-gel,spark plasma sintering

88 - ABS 867

SYNTHESIS OF $Bi_4Ti_3O_{12}$ COMPOUNDS VIA CITRATE METHOD

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Ferroelectric-piezoelectric ceramics generate intense force with a rapid response at high frequencies. Most piezoelectric materials used by industry are lead-based, such as perovskites Pb(Zr, Ti)O3 (PZT), where lead is a highly toxic element and its use is regulated globally. Piezoelectric ceramics based on niobates and lead-free titanates are some examples of lead-free piezoelectric in their composition. Bi4Ti3O12 has been largely studied recently due to its good electromechanical properties, being able to compete with PZT ceramics, especially for high temperatures applications. The synthesis of high quality Bi4Ti3O12 ceramics is, however, challenging due to Bi volatilization, leading to the formation of second phases and non-stoichiometric compounds, lowering its piezoelectric properties. Here, ceramic powders are synthesized using a chemical route known as Citrate Method. Characterization studies were made by Simultaneous Thermal Analysis, X-Ray Diffraction, Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy, in order to check the composition, morphology and present phases in the samples. The calcination process was carried in air at 500, 600, 700 and 800 °C, producing nanometric ceramic powders (~100 nm) with a single phase and high purity. At lower calcination temperatures the metastable Bi2Ti2O7 phase is present at a low mass fraction (< 5%),. However, this is eliminated when heat-treated at temperatures higher than 700 °C. Rietveld refinement shows that the increase in the calcination temperature leads to a cell volume closer to theoretical values, indicating a relaxation the crystal structure due to defects elimination. EDS analysis shows a Bi/Ti ratio of 1.44, a close value to the calculated (1.33). The observed Bi/Ti ratio did not change with an increase of the calcination temperature, indicating the suppression of Bi volatilization. The synthesis here presented has shown impressive results, is an excellent option for the production of high quality Bi4Ti3O12 powders.

Keywords: piezoelectric, bismuth titanate, lead-free

89 - ABS 78

POLING PROCESS EFFECT OVER STRUCTURAL AND MICROSTRUCTURAL CHARACTERISTICS OF BCTZ (X=0.15) CERAMICS

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In recent years the scientific interest on lead-free electroceramic materials has increased considerably due to the potential impact that these materials have over many industrial applications. BCTZ (Ba1-xCaxTi1-yZryO3) ceramics have shown to be optimal candidates for different electronic applications, derived from their high dielectric, piezoelectric and ferroelectric activity. Moreover, stoichiometries compositions situated near the morphotropic phase boundary (MPB) exhibit a high electrical response, as a result of the low energy barriers for the spontaneous polarization rotation or deformation in the presence of an external electric field (poling), which allows the movement of the ferroelectric-ferroelastic domain walls, promoting a preferential orientation in the ceramic material. The present work shows the effect of the poling process on the structure and microstructure of BCTZ ceramic materials through the application of an external electric field. The structural analysis was carried out by X-ray diffraction, confocal Raman microscopy and imaging and scanning electron microscopy. Upon application of an electric field, the E(LO3) +A1(LO2) +E(TO4) mode of the Raman spectra shifts to lower frequencies, indicating a reduction of the bonding force between the ions at the B-site of the perovskite (Ti4+, Zr4+) and the oxygen ions of the octahedron for the poled samples. Besides, the spatially resolved mentioned mode of the Raman spectra shows a narrower distribution in the poled sample, monitoring the strong effect of alignment of the polarization in the direction of the field. These characteristics are related with a complex ferroelectric domain distribution. The polar structure change after the application of the electric field is revealed as well by the changes on the dielectric permittivity curves as a function of the temperature. The aim of this work is to extend the knowledge about these ceramic materials in order to be used in various technological applications.

Keywords: Lead-free electroceramics, Poling process, Morphotropic phase boundary

90 - ABS 863

POROUS FERROELECTRIC CERAMICS FILMS FOR ELECTRONICS APPLICATIONS

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Porous ferroelectric films with a random or regular pore structure are the very prominent media for different kinds of electronic devices: MEMS, pyroelectric detectors, energy harvesting, memory, etc. They can be also used for creation of composite structures to obtain new physical phenomena in the neighboring materials and at their interfaces, e.g. ferroelectric/magnetic, ferroelectric/semiconductor, piezoelectric/piezoresistor, etc.

Sol-gel techniques are very attractive methods to produce porous films with different internal structure, see e.g. [1]. Typically, porous structure is formed by addition of porogens – organic substances which are destroyed during the heat treatment, leaving empty pores. In this work we discuss properties of different kinds of porous ceramic PZT films obtained by two main sol-gel approaches. The first one is based on the use of polyvinylpyrrolidone (PVP) with different molecular weights and concentration as a porogen. It will be shown that porous films with a fairly large pore diameter of 30-80 nm and 3-0 or 3-3 connectivity can be obtained in this way. The films demonstrate attracting electrical properties, for example polarization and coercive field degrade with the porosity increase not as intensive as theory for bulk volume ceramics predicts. The reason is the mechanical stress relaxation as it was confirmed by X-ray study. To clarify mechanisms of conductivity the transient currents technique was applied [2].

The second way for preparation of porous materials is evaporation induced self-assembly (EISA) process. Different kinds of surfactants were used as a template. It was shown that this process results in a very small pore size of several nanometers. As a result, the PZT films with extremely high perovskite texture can be produced in this way.

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Keywords: ferroelectric thin film, porous ferroelectric ceramics, sol-gel

91 - ABS 959

PIEZOELECTRIC PERFORMANCE OF VERTICALLY ALIGNED CUBIC-PHASE $BaTiO_3$ NANOPARTICLES

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In general, particle-polymer composite nanogenerators, in which the particles are dispersed in the polymer matrix, are less power generation than the oriented particle composite because of the particle randomness and a thick insulating polymer layer. If the nanoparticles are unidirectionally oriented in a polymer matrix to form a bundle of chains, the stress-induced energy can be more concentrated and easier transferred to the electrodes. Here, we present a facile electrical orientation method to obtain vertically aligned BaTiO3 nanoparticle arrays in a polymer matrix for the improved piezoelectric power generation. Compared to the randomly dispersed nanoparticle composite, the vertically aligned BaTiO3 array film has an excellent electrical output performance (ca. 3 V and 650 nA) and more than twice the transparency because of reducing light scattering by gathering BaTiO3 nanoparticles. In addition to the improved piezoelectric performance and transparency due to the alignment of the nanoparticles, we found that the (200) diffraction plane of BaTiO3 is transformed by an electric field. Furthermore, it is demonstrated that electric power generated by a mechanical micorloading of 4 micrometer denting depth using a nanoindenter equipment can pass through the polymer insulating layer in the well-aligned composite system but no the dispersed system.

Keywords: Electric Field, Barium Titanite, Piezoelectric

92 - ABS 13

ENHANCED MULTIFERROIC PROPERTIES IN BCZT/LCMO LAMINATED COMPOSITES PREPARED BY PLASMA ACTIVATED SINTERING

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Multiferroic magnetoelectric (ME) composites have been attracting much attention due to the significant applications for spintronics devices, high sensitive sensors, storage and so on. The ME effect was initially observed as an intrinsic effect in single-phase multiferroic materials, but those materials are limited because their ME effect only occurs at low temperature or is too weak to practical applications. The artificial magnetoelectric composites composed of ferroelectric and ferromagnetic components could be the promising candidates for producing strong extrinsic ME effect. Lead-free Ba0.85Ca0.15Zr0.10Ti0.90 (BCZT) and La0.67Ca0.33MnO3 (LCMO) were then selected as the ferroelectric and ferromagnetic phases, respectively, to prepare a new kind of BCZT/LCMO laminated composites. The structure, dielectric, ferroelectric and magnetoelectric properties of the laminated composites were mainly reported.

BCZT/LCMO laminated composites were prepared by Plasma Activated Sintering (PAS), using the BCZT and LCMO ceramic discs with differernt thickness ratios. The BCZT and LCMO discs were first ground and polished into proper thicknesses and then sintered at 1000 °C by PAS under a pressure of 50 MPa for 10 min. Then the composites were annealed in air at 900 °C for 5 h. Finally, the microstructure and properties of the composites were measured by SEM, TEM, quasi-static d33 meter, LCR meter and ME measurement system.

A perfect bonding of BCZT/LCMO interface without structural defects was obtained, with the aggregation of Ca element at the interface. The ferroelectric and ferromagnetic characteristics demonstrated that the laminated composites were multiferroic in nature, and their performances showed strong dependence on the thickness ratio of BCZT to LCMO. With the increase of LCMO content in the laminated composites, the piezoelectric coefficient and coercive electric fields decreased, while the saturated magnetization increased and coercive magnetic field remained almost unchanged. The obtained remnant polarization, coercive electric field and magnetoelectric coefficient of the composites were found to be 10.1 μC/cm2, 1.97 kV/cm and 2.65 mV/cm•Oe, respectively. Enhanced dielectric properties ($\varepsilon r = 7217$, $\varepsilon m = 25097$ at 1 kHz and room-temperature) were achieved in the BCZT/LCMO laminated composites, which could be attributed to the contribution of ferromagnetic LCMO and the Maxwell-Wagner model.

In summary, multiferroic BCZT/LCMO laminated composites with different thickness ratios had been successfully prepared by Plasma Activated Sintering. A perfect bonding and defect-free BCZT/LCMO interface was obtained, and the enhanced multiferroic properties was observed. All these results indicated BCZT/LCMO laminated composite as a promising material for multiferroic composite.

Keywords: BCZT/LCMO, Laminated composites, Magnetoelectric coefficient

93 - ABS 846

NEW APPROACHES FOR REPLACING COBALT IN BLUE GLAZES

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This work had the objective of replacing cobalt compounds used as dyes in the formulation of the blue glazes for application in porcelain stoneware flooring. It was also required that this substitution did not cause significant changes in the characteristics of the glaze or the final product.
For this purpose, a transparent frit and mixtures of three compounds containing copper were used to prepare glaze suspensions which were applied in porcelain stoneware tiles and then fired to a maximum temperature of 1200 °C.
It was not possible to obtain glaze formulations for porcelain stoneware with blue coloration without the addition of cobalt. However, compositions with small cobalt addition to the mixture of the copper-containing compounds allowed to obtain glazes with a blue colour close to the desired one, without causing changes in the characteristics of the base glaze, namely at the chemical and abrasion resistance levels.
The formulation that showed, simultaneously, the smallest colour difference when compared with the reference sample and the lowest amount of cobalt was obtained for a mixture with a reduction to 1/8 of the mass of the dye with cobalt, which represents an economy in the costs with dyes of about 60%.

Acknowledgments
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES

Keywords: Glazes,Blue,Cobalt

94 - ABS 281

DEVELOPING TESTS FOR FLAMEPROOF TABLEWARE

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The interest in either tableware ceramics usable directly on a stove, for heating or cooking food, has been growing. [1] Under such conditions of use, ceramics need to withstand as many cycles as possible of heating to some high temperature, kept at those temperatures for a while and then cooled again to room temperature. This is a case different from thermal shock resistance, since during heating the temperature is not uniform all over the pieces under use. The materials must be instead flame resistant and tests are need to help the quality control of production.

It was recently shown that stoneware ceramics with low thermal expansion withstand more than 50 flameproof cycles if filled with water. [1] In this case, the radial difference in temperature (difference between the middle and the flame zone) is readily setup and lower than 5 °C due to effect of boiling water temperature. This will be different if oil is used or if food is simply heated up in the ceramic. Therefore, it is important to proceed with the development of tests suitable for flameproof ceramics. The aim of this work is to analyse the maximum radial temperature a ceramic withstand without failure.

Stoneware ceramics were used for the experiments, in the same conditions as in [1], without the introduction of water. Heating was carried on up to the failure of the pieces, registering the temperature at different points. Samples of unused pieces were prepared for mechanical strength, determination of Young's modulus, dilatometry and optical microscope observations. It is possible to calculate the rupture stress by using the radial temperature difference, since the material is brittle in the temperature range of experiments. The stress values obtained in this way are in very good agreement with mechanical failure by crack propagation with initial sizes of the order of 250 um. This matches the length of surface cracks observed in the glaze.

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Keywords: Flameproof Tableware, Tests, Stoneware

95 - ABS 822

LIGHTWEIGHT SILICATIC AGGREGATES FROM AGRO-FOOD INDUSTRY RESIDUES AND POST-CONSUME AS AN OPEN-LOOP RECYCLING OPTION

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Open-loop recycling is any recycling process where the recycled materials are converted into both new raw materials and waste product. Typically, materials recycled through open-loop recycling go on to be used for purposes different from their former, pre-recycled purpose. An important field of application is represented by agricultural sector. On one hand, continuing population growth, increasing consumption are driving global food demand, with agricultural activity expanding. Further, modern agriculture rapidly improves productivity, meanwhile it pays heavy prices such as consumption of resources and energy and damages to the agricultural environment. The modern agricultural system is wasteful, for example with Europe generating about 700 million tons of agrifood waste each year.

Nowadays, the production of light aggregates known as LWAs (Lightweight Aggregates) is increasing exponentially because they have several applications such as geotechnical fill, insulation products, soil engineering, hydro-culture, drainage, roof gardens and filter. Actually, one of the major issues that needs to be a concern is to minimize and recycling industrials wastes for the production of new materials thus avoiding exhausting of natural resources. LWAs, comparable to commercial ones such as Light Expanded Clay Aggregates (LECA®), present additional and improved functionalities such as a good capacity of water retention thus avoiding an excessive consume of this primary resource.

In the present study, light silicatic aggregates were produced using waste from the agro-food sector and/or post-consume in order to obtain materials for agronomic use with a controlled release of nutrients and high water absorption. The materials were tailored with and without a glass properly formulated and carrier of P and K nutritive elements. These materials were obtained using local clays from Spain and Italy in line with km 0 concept. Chemical-physical characterization of the prototypes obtained was performed, together with a first environmental impact (Carboon Footprint and LCA studies) and plant (Ocimum basilicum or sweet basil) growth estimation for lightweight aggregates that could be used in green roofs, hanging gardens and crops.

Keywords: Lightweight silicatic aggregat, agro-food industry residues, open-loop recycling

96 - ABS 191

CHARACTERIZATION OF REFRACTORIES MADE FROM STEEL PRODUCTION SLAG FOR THERMAL ENERGY INTENSIVE INDUSTRIES

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Objective: The European steel industry generates millions of tons of slag as a by-product resulting from steel making. About 24% of this residue is not being reused, representing a severe environmental problem in Europe, but also a huge amount of available material. The main goal of this study is to investigate alternatives to turn slags from steel industry into valuable and low-cost feedstock for the production of refractory materials.

Materials & Methods: Different types of insulating refractory materials needed in all thermal energy intensive industries, for example in the construction of furnaces, kilns, incinerators, or reactors, were considered. Technical requirements set for slag based refractory materials were mechanical and chemical resistance up to 1200 °C in gaseous atmosphere.
Ferrochrome slag (FeCr) in the form of fine aggregates of 0-4 mm in size was tested in this study. Commercially available calcium aluminate cements were used as binder. As fine fraction material, other steel industry by-product, EAF slag, was selected for investigation. As a reference, commercial refractory castable was used. Laser flash analysis was carried out to measure specific heat capacity, thermal diffusivity and thermal conductivity of the samples. Thermal expansion coefficient, α, was measured by dilatometry. The microstructure and crystalline structure of the new materials were characterised by SEM and XRD analyses.

Results: The calculated average thermal expansion coefficient (α = 8.5 x 10-6 K-1), is comparable to commercially available refractory materials designed for similar targeted applications (α = 6.8 x 10-6 K-1). The values of specific heat were confirmed slightly increase with higher testing temperatures (up to 1000 °C).Thermal conductivity values were relatively low, in all cases lower than the values of the commercial reference (2.51 W/m*K). The exploitation potential of different insulating refractory materials made from slag will be discussed.

Conclusion: The production of insulating refractories based on slag materials should be considered further for their use in thermal energy intensive industries. The present approach opens up new possibilities and opportunities for an economical recycling of steel slag.

Acknowledgement: This research has received funding from the European Union's H2020 programme Waste-1-2014, project RESLAG (GA-642067).

Keywords: refractories, slag, thermal energy

97 - ABS 788

BIODIESEL CONVERSION WITH GEOPOLYMER POWDERS AND 3D LATTICES

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Many environmental problems are caused when fossil fuels are used in engines. Thanks to its similar properties, a promising substitute for this kind of fuel is biodiesel (fatty acid alkyl esters), that is renewable, biodegradable and not toxic. The most used process to prepare biodiesel is by homogeneous transesterification of vegetable oils, even though it produces a high concentration of impurities in the product. The use of heterogeneous catalysts is quite attractive, their main advantage being that the purification step is minimized.

This work investigated geopolymers (GP) acting as heterogeneous catalysts to produce biodiesel by the transesterification reaction of soybean oil with methanol. Three types of GP powder were produced mixing metakaolin with an activating alkaline solution: Na-based, K-based GP and a mixture between them; they were treated at 110, 300, 500 and 700 °C, then lattice-shaped GPs were designed and produced by DIW, adding PEG and filler in the previous formulation and then, they were dried at 110 °C. Porous structures with Ø ~24 mm x 9,6 mm height and unsupported parts were produced. All materials were characterized. The transesterification reaction was carried out using all the samples as a heterogeneous catalyst to evaluate the yield of biodiesel.

According to the results obtained, it was verified that using GP both in powder and structure as a catalyst, it was possible to obtain biodiesel from the transesterification of soybean oil. Comparing the materials with the same molar ratios, Na.K_GP treated at 500°C (powder) achieved the highest conversion (~98%). For the 3D structure tested in the reaction (3D_Na_GP1, 110 °C) a conversion was observed, but lower (~41%) compared to Na.K_GP, even in its powdered version (~53%).

Keywords: Biodiesel, Geopolymer, Heterogeneous catalyst

98 - ABS 706

INVESTIGATION OF THE EFFECT OF FELDSPAR AND PHYLLOSILICATES ON MOISTURE EXPANSION IN WALL TILE

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In ceramic wall tile production, raw materials consisting of illite, chlorite, kaolin and quartz, feldspar (albite - sanidine-orthoclase) calcite and dolomite are widely used. During the heating of these raw materials, a series of transformations determining the final properties of ceramic products occurs. Throughout the ceramic process, these crystal phases -when the stability limits are exceeded- -are partially dissociated and others are formed simultaneously. The amount of calcite is the determinant of the new phases formed. In the recipe compositions with high calcite content a formation of gehlenite and calcic plagioclase has been observed (1).

The phyllosilicates, or sheet silicates, are an important group of minerals that includes the micas, chlorite, serpentine, talc and the clay minerals. The disintegration of phyllosiliciates through dehydroxylation assists in nucleation of phases of the high-tempreature crystal.

Amorphous phases generally arising from the decomposition of clay minerals during the firing tend to result in high moisture expansion due to high surface energy and specific area that they provided. The glass phase is formed by the partial melting of feldspar existing in the raw materials used in the recipe. The feldspars start to melt at 1000 -1150 °C according to their structures. A significant reduction in porosity and a considerable reduction in the average radius of the pores take place with the beginning of vitrification.

In this study, the effect of changing the feldspar and phyllosilicate ratios on the moisture expansion was determined by keeping the amount of calcite used in the wall tiles. The impacts of changing of feldspar and phyllosilicate ratios by holding the amount of calcite used in the structures of wall tiles as stable- over the moisture expansion are examined in this study. To this end, XRF analyzes were performed in order to determine the chemical composition of the samples obtained by preparing prescriptions at different rates; the mineral structures were illuminated through XRD analyzes and tiles the moisture expansive measurements of which had been carried out were put to the autoclave test (6-3,5h ~ 155°C) The autoclave test was performed to observe the working performance of the wall tile. In the aftermath of autoclaves warm and -after 1 day curvature- a deviation from the square and the smoothness of the edge were measured. At the end of the studies carried out, it was observed that the moisture expansion values varied between %0.015 - %0.065.

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Keywords: Moisture Expansion, Ceramic Wall Tiles, Phyllosilicates

99 - ABS 674

GEOPOLYMERIC COMPOSITES BY RESIN TRANSFER MOULDING

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Geopolymers are a class of materials that can be obtained by reticulation of aluminosilicates on specific conditions of pH and chemical stoichiometry. This reaction results in an amorphous or semi-crystalline consolidated, which can also be defined as an inorganic polymer. These materials are obtained at low cost, both because the feedstocks are sources of aluminosilicates such as clay or fly-ash, and the processing requires lower energy compared to the conventional processing of polymers or ceramics. The inorganic nature of geopolymers provides their attractive properties, such as thermal stability and fire resistance, but also affects their mechanical properties, which can be a limitation for some applications. In this study, a geopolymeric matrix was reinforced with fibers as a secondary phase to provide toughness and improved mechanical properties, while maintaining thermal properties suitable for a wide range of applications. Alkali-activated metakaolin was used as matrix along with various types of fibers to create the composites, manufactured by resin transfer moulding (RTM). A specific geopolymer composition was formulated to achieve the optimal viscosity for the chosen industrial process and equipment. The ratio K/Al = 1,2 was used to obtain the best rheology for the infiltration, and a Si/Al = 4 ratio was used to obtain a stable geopolymer network. Mechanical tests, thermogravimetry, variation of pH and density measurements were carried out to evaluate the effect of the second phase addition in the matrix, as well as SEM analysis to understand the interaction between matrix and fibers. The addition of fibers resulted in an enhancement of up to 50% in flexural strength. For aesthetic purpose, colouring of geopolymeric composites was tested as well, using either organic and inorganic pigments.

Keywords: Geopolymer, Composites, Fiber

100 - ABS 665

STABILIZATION OF <BETA>-DICALCIUM SILICATE

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Dicalcium silicate (Ca2SiO4) is used in different domains, such as bioceramics and cement. For biomedical applications, the interest is to obtain the beta polymorph [1]. In the cement field, belite (Ca2SiO4 + dopants) clinker appears as one of the most promising route to reduce CO2 emission in the cement industry [2]. Five polymorphs can be obtained as a function of temperature and β is of most interest in the cement field due to its hydraulic activity. Since the γ-polymorph stable at room temperature has no hydraulic activity, the stabilization of β-polymorph becomes essential. This paper explores how the processing parameters can induce specific twinning morphologies and surface relief which stabilize the β-polymorph.

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Keywords: Ca2SiO4,Stabilization,Twinning morphologies

101 - ABS 637

CERAMIC WASTES AS PRECURSORS FOR NEW ECO-FRIENDLY BUILDING AND RESTORATION MATERIALS

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First results of ceramic waste use as geopolymer precursors are shown in this research as part of the AGM project (Advanced Green Materials for Cultural Heritage, fund by MIUR within National Operation Program for Research and Innovation 2014-2020). Ceramic waste are one of the main source of waste in Europe (1) and represent an ordinary problem for brick industries. Converting them in new products that can replace high energy consuming building/restoration materials is the challenge of this century. Furthermore in the current severe environmental conditions a serious damage of the ancient architecture, especially those of Roman time, mainly made by red-clay bricks, is evident. This makes urgent to find new compatible and durable restoration products (2, 3). In this context geopolymers seem to be the materials of the future, indeed they reach high performances maintaining low energy consuming production and can be diversified according to the specific application (4). Commonly the implementation of geopolymers starts from kaolinitic clay, volcanic ash, fly ash or blast furnace slag, while the investigating of ceramic waste as geopolymer precursors is still beginning (5). With this research we want to light up the potentiality of ceramics for this purpose, starting from hollow brick and glazed tiles waste retrieved from local industries. After their mineralogical and chemical characterization (XRD, XRF and Raman spectroscopy), numerous geopolymeric formulations were tried and the quality of the resulting products were investigated. In order to find the best setting, the formulations were tested changing from time to time the following parameters: granulometry of the raw materials, type and dosage of alkaline activators, curing conditions - room temperature and different thermal treatments: low temperature for prolonged time (65°C, 7 days) (6), high temperature for short time (100°C, 48 h; 400°C, 24 h) (7) - and percentage of a second component in the mixture (metakaolin). Comparing the results of the different mix designs it was possible to individuate what the changing parameters determines in the final product and some promising mix designs, basis for future developments. A positive answer is given, also, by the workability of these new class of materials, fundamental requisite in restoration interventions. The potentiality of ceramic waste to produce geopolymers and their feasibility for application as building and/or brick masonry restoration materials (8) is enhanced by these encouraging results.

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Keywords: Geopolymers, Cultural Heritage, C&D Waste

102 - ABS 602

THE COMPARISON OF ADDITION IMPACT OF HALLOYSITE AND KAOLIN ON THE PROPERTIES OF THE CERAMIC INTUMESCENT COATINGS

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The intumescent coatings are example of the materials protecting against fire. When the protective layer is exposed to the fire, it softens and releases indifferent chemically gases that simultaneously cause intumescent of coating. Then it is charred, forming a rigid pumice-like structure, which acts as a thermal insulation. Softening, evaporation, decomposition etc. draw heat from the environment, whereas the pumice structure insulates the material against excessive temperature rise. Traditional intumescent system consists of a binder, carbonizing substance, dehydrating agent and blowing agent. Additionally, ceramic fillers, which could improve efficiency and resistance of the porous layer, are also added.

The coatings, which consisted of epoxy resin, melamine, pentaerythritol and ammonium polyphosphate, were prepared. To achieve better thermal and intumescent properties, other compounds such as halloysite and kaolin were also applied. The influence of the halloysite/kaolin addition on the intumescent size as well as its compactness and adhesion of the coating to the substrate were compared. Suitable fire tests and thermal analysis (TG/DSC) were done. MIR and SEM analysis helped to described the intumescent mechanism.

Keywords: intumescent coatings, fire protection, halloysite

103 - ABS 557

GLASS-CERAMIC FOAM – USABILITY OF VITRIFIED WASTE FROM PLASMA SMELTING PROCESS

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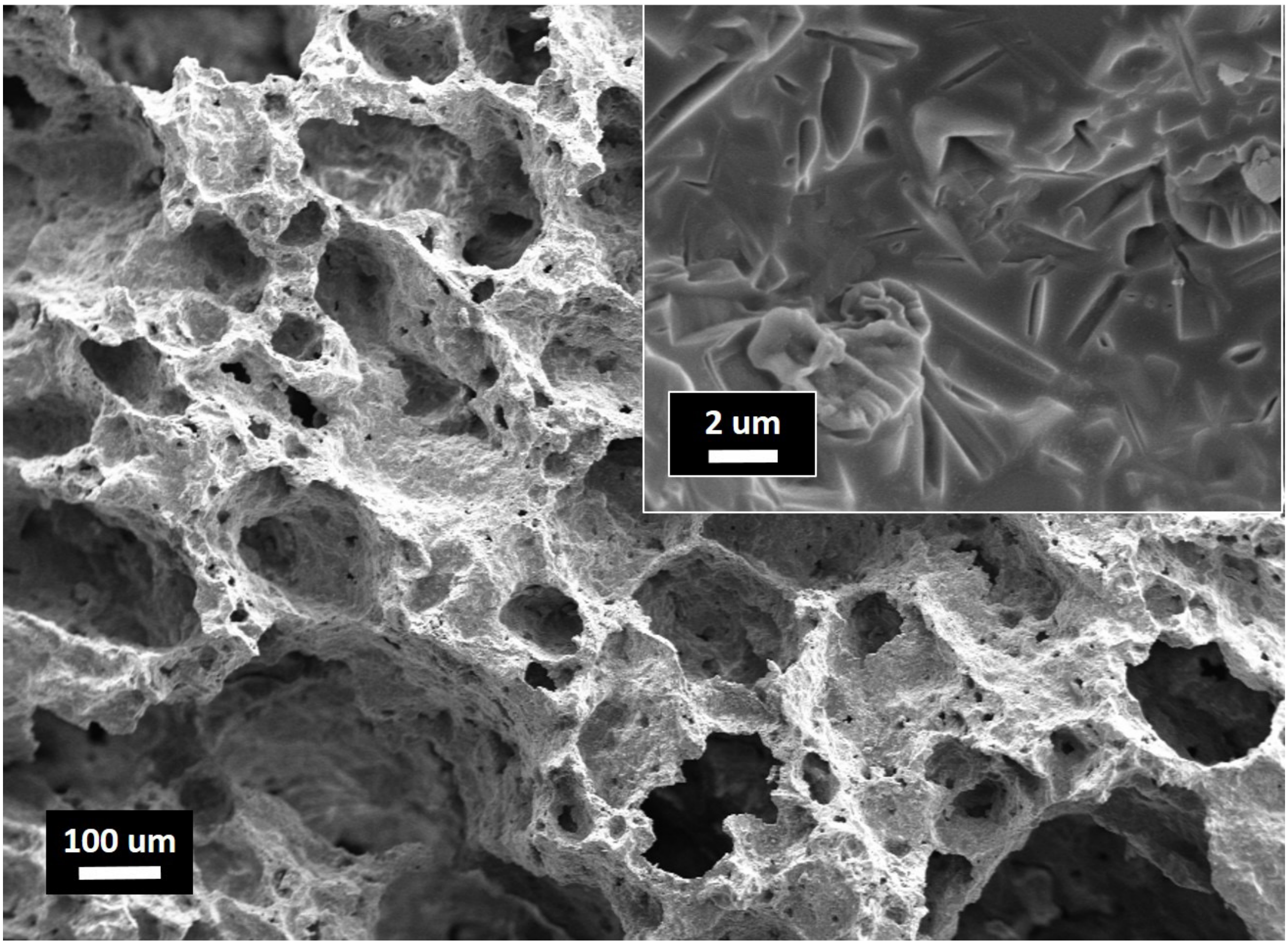
The work report on experimental results obtained from the production the glassy slag by plasma smelting of two different wastes mixture. Combination of two wastes with different chemical composition is promising way how to optimize the energy consumption in the disposal process. Asbestos-cement roof tiles and fly ash from fluidised-bed boilers (with weight ratio of 1:1) was used for preparation of glassy (vitrified) slag. The thermal process facilitated the 14.4 wt.% reduction of the weight of the original mixture of waste and the 72 vol.% volume reduction.

Glassy slag is then adopted as the raw material in the production of porous materials intended for various architectural applications, eliminating thus its further disposal necessity. Formation of porous glass-ceramic matrix, using the vitrified slag containing $CaSO_4$ as the pore-forming agent, is described in detail. Glass-ceramic foam, formed by rapid heating of the mixture of glassy slag and 1 wt.% of $CaSO_4$, with 66% porosity, consists of crystallized calcium aluminosilicate ($Ca_2Al_2SiO_7$, $Ca_{0.88}Al_{1.77}Si_{2.23}O_8$). The thermal conductivity of the prepared porous material, measured by the laser flash thermal analysis, is 0.22 W/mK.

Keywords: glassy slag, porous material, glass ceramics



104 - ABS 511

INVESTIGATION OF THE USE OF KARADORU AND SOGUCAK LEUCOGRANITES (BIGA PENINSULA, KB ANATOLIA) IN PORCELAIN TILE PRODUCTION

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Porcelain ceramic tiles are produced from a mixture of ball clay, kaolin, quartz and Na- and K-Feldspars. Gradually increase in this type production, the consumption of the natural raw materials increases rapidly. This situation leads the ceramic tile producers to look for alternative raw materials close to the plants. In this context, a series of analytical studies were carried out on two leuco granites of the Biga Peninsula, which were not used as raw materials. Characterization of leuco granite samples were used by the XRF and XRD methods, and DTA/TG analysis for thermal behavior were performed. The rheological behavior of the material and its physico-mechanic aspects such as firing shrinkage, water absorption, dry and fired strength and color were investigated in detail. The results obtained from these analyses indicated that Karadoru and Sogucak leuco granites could be used as fluxing materials. Therefore, the feldspatic raw material contents used in standard recipes are gradually reduced and new formulas have been created by adding different ratios of leuco granites. Firing tests were carried out to determine the behavior of these new raw materials in new recipes. The new occurred mineral/glass phases and microstructures formed in the fired tablets were examined by XRD and SEM. Beside this, sintering aspects were also documented by non-contact dilatometer. In addition, the physico-mechanical properties, water absorption, color (L, a, b) and strength tests of the newly formed bodies were studied and compared to the standard bodies.

All these findings led to us that the Karadoru and Sogucak leuco granites can be used for Na-Feldspar alternative, and used in porcelain tile production as a flux material in different rates. Usage of these and similar local raw materials will reduce the amount of raw materials supplied far from the plants and also reduce their costs. On the other hand, it will promote the use of leuco granitic rocks (aplogranites, aplites, etc…) which are not used currently, as potential ceramic raw materials.

Keywords: Leucogranite, Fluxing agent, Na-Feldspar alternative

105 - ABS 497

ANTIBACTERIAL PROPERTIES OF TRADITIONAL CERAMIC GLAZES CONTAINING COPPER OXIDE OR IRON OXIDE

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Traditional ceramic glazes formulated with copper oxide (CuO) or iron oxide (Fe2O3) exhibited antibacterial properties on Staphylococcus aureus (Gram Positive) and Escherichia coli (Gram Negative). All the ceramic glazes containing CuO or Fe2O3 (above 1 w/o) showed antibacterial behavior when fired in reducing atmosphere. However, some of copper glazes presented antibacterial behavior and iron glaze had no antibacterial properties at all when sintered in an oxidizing atmosphere. To elucidate the antibacterial mechanism, ceramic glazes were studied for phase analysis, dissolution behavior and surface zeta potential. Metallic copper was precipitated on the surface of glaze when sintered in reducing atmosphere or in oxidizing atmosphere above 5 w/o CuO addition. Less than 0.05 ppm of Cu or Fe ions was dissolved from glazes. Ca ion was most dissolved among all the samples. Especially, the highest dissolution of Ca ion (0.69 ppm) was shown from the iron glaze fired in reducing atmosphere. Glaze surface was highly negatively charged when sintered in reducing atmosphere compared to the samples sintered in oxidizing atmosphere. The antibacterial behavior of ceramic glazes seemed to be directly related to the dissolution behavior of cations, but the antibacterial behavior of oxidized specimens was not explained by the dissolution behavior. Surface potential of ceramic glazes appeared to play an auxiliary role in antibacterial properties.

Keywords: Glaze, Antibacterial, Sintering

106 - ABS 472

THE INFLUENCE OF THE TOTAL POROSITY AND MOISTURE EXPANSION OF SILICATE CERAMICS

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Roof tiles do not only embellish the house, but they mainly serve to prevent rainwater from entering the house. Water penetrated through pores can cause damage in the liquid and solid state. The higher the porosity, the more water can penetrate. In winter, the water in the pores can freeze and cause damage. Moisture expansion is also influenced by wetness (e.g. [1]) and over time can result in cracks and spalling due to material expansion.

This shows that total porosity and moisture expansion are very important parameters of (freeze) -resistance of roof tiles. Both parameters correlate if the chemical/mineralogical composition is constant and only the firing temperatures change. Investigations with firing temperatures from 940°C to 1080°C have already shown this. By changing the chemical composition (additives of alkaline earth/alkali rich compounds) at constant firing temperature (tests with firing temperatures of 1050°C, holding time 1h, total firing time 15,8h), no correlation between total porosity and moisture expansion can be detected. Further investigations have shown that the mineralogy in roof tiles, in addition to the firing temperature and firing time, has a large influence on the pore formation during the sintering process. The mineral content in the ceramic body determines not only the porosity but also the moisture expansion. Investigations show connections between mineralogy and moisture expansion [2]. Thus the moisture expansion in the silicate ceramics can be influenced by means of targeted admixtures (alkaline earth/alkali rich compounds; e.g. [3]) to the clay plant.

The aim of further investigations is to find out the perfect firing conditions (temperature, time) and types of chemical additives (also mixtures of individual additives) as well as percentages, which have a positive effect on the total porosity and simultaneously on the moisture expansion in the ceramic body. Thus, if the chemical/mineralogical composition of the respective individual clay plant is known, the firing parameters and admixtures can be specifically adapted to achieve optimum results in the resistance of the roof tile.

[1] VASIC, R. & VASIC, M. (2011): Phenomenon of moisture expansion and its influence on mechanical properties of brick clay products. – Ceramic Materials, 63 (1), pp. 54-57.
[2] COLE, W.F. (1968): Some relationships between mineralogical and chemical composition and moisture expansion of fired clay bodies. – J. Aust. Ceram. Soc., 4 (1), pp. 5-9.
[3] ABDRAKHIMOV, V.Z., ABDRAKHIMOVA, E.S. & ABDRAKHIMOV, D.V. (1998): Moist expansion of ceramic materials. – Glass and Ceramics, 55 (9-10), pp. 285-287.

Keywords: roof tiles, total porosity, moisture expansion

107 - ABS 435

SYNTHESIS AND CHARACTERIZATION OF SELF-SUPPORTING ZEOLITES BY GEOPOLYMER GEL CONVERSION FOR WATER SOFTENING

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In several industrial applications, such as water softening, supporting or shaping powdery zeolites is a technological urgency. Zeolites, such as Na-A and Na-X are employed to a large extent as water softeners, since they can exchange their sodium ions with “hard water ions”, such as calcium and magnesium. Moreover a synergistic effect can be reached using a mixture of them.

In the present work, a self-supporting zeolitic filter was synthesized by geopolymer gel conversion using a one-step procedure, which realizes simultaneously geopolymerization and crystallization under mild operating conditions (40°C), without further treatments. The geopolymer gel precursors were prepared by mixing metakaolin, silicon powder and sodium hydroxide solution. The geopolymer conversion generates a hierarchical porosity characterized by mesoporosity (typical of the geopolymer matrix) and microporosity (characteristic of the zeolitic phases), while the addition of the silicon powder is intended to widen the porosity of the sample also to the macro range. The specimens obtained after 3 days of curing or more showed the presence of two distinct phases, identified as zeolites Na-A and 13X, the relative quantity of each phase being strictly related to the experimental conditions used. The microstructure presented well-developed zeolite Na-A crystals with cubic-like morphology and a mean dimension of 1.5 μm. Na-A crystals seem to be surrounded by smaller nanometric crystals with the typical morphology of faujasite zeolites. It seems that the porosity generated by foaming process promotes the zeolite nucleation mainly on the surfaces of the pores, whereas the struts remain amorphous. The cation exchange capacity of the geopolymer self-supporting zeolite resulted to be 3.32 meq/g. As regards the water softening capacity, the amorphous surface of the geopolymeric struts can exchange cations to some extent, but also to adsorb them, while the crystalline zeolitic surface of the pores is mainly able to exchange cations, with a faster kinetic and a higher affinity toward magnesium.

The presence of a geopolymer backbone support and shape the zeolitic powder widening its technological application field. So, such specimens can be proposed as membranes or filters for ion exchange processes in aqueous solution.

Keywords: geopolymer gel conversion, zeolite, water softening

109 - ABS 385

BEHAVIOUR OF PALYGORSKITE NANOTUBES APPLIED TO THE TREATMENT OF NUCLEAR EFFLUENT

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Clay and clay minerals, modified or not, will be recognized as 21st century materials due to their abundance, low cost, applicability and environmentally friendly. Natural Palygorskite clays show suitable physical and chemical properties and characteristics to use this material like potential nano-sorbent and like immobilization matrix aiming the concentration and solidification of radionuclides present in nuclear wastes, respectively. In the process of developing materials with sorption properties for the incorporation and subsequent immobilization of radionuclides in the same matrix, the most important steps are the generation of active sites, together with increased specific surface area and the suitable heat treatment that produces the structural folding. This study evaluated determinant parameters and conditions for the activation process of the natural Palygorskite nanotubes aiming to the sorption of radionuclides of interest in the structure of nanotubes and subsequent evaluation of the parameters that involve the structural folding by heat treatment. The results obtained of maximum sorption capacity for nickel on activated natural nanotubes are very promising. By this study is verified that the optimization of the acid activation process is fundamental to improve the sorption's capacities for specifics radionuclides by activated natural nanotubes.

Keywords: Palygorskite, natural nanotubes, nuclear waste

110 - ABS 221

ANTIBACTERIAL APPLICATION OF NOVEL MicNo® PARTICLES FOR TRADITIONAL CERAMIC BODIES

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Traditional ceramic materials such as tiles and sanitarywares, which we are in contact with in a significant part of our daily lives, offer ideal living areas by accommodating some dangerous microorganisms, even if we are not aware of them. Whether in our kitchen in our bathroom, and especially in the common areas where we cannot be sure of its cleanliness, bacteria that we may be exposed to endanger our health seriously. While we provide the necessary hygienic conditions with various methods to protect our health, it should be considered as a more permanent solution to give antibacterial properties to the ceramic surfaces, we touch. Antibacterial surfaces, which are obtained by coating the surfaces of ceramic materials with antibacterial agents or by adding antibacterial agents to the glaze composition during the production, offer the expected hygienic solution by preventing or killing the bacteria such as Escherichia coli (ATCC 8739) and Staphylococcus aureus (ATCC 6538). In addition to the widely used Ag and Cu metallic ions, inorganic compounds such as Bi2O3, CuO, SnO2, TiO2 and ZnO are also used when forming hygienic surfaces. The antibacterial effect of nano Ag, which is typically higher than other antibacterial materials, is used in large quantities for effective protection against microorganisms in glaze compositions. It is known that the cost of nano Ag is high and the whiteness of the glazes with embedded Ag particles is sacrificed at the end product. In this study, modified formed of designed ZnO-based particle technology known as MicNo® worldwide is proposed as an alternative to the widely used nano Ag as antibacterial active component in sanitaryware applications without negatively influencing the surface properties of glazes. Here, modified designed MicNo® powders were added to ceramic sanitaryware glaze recipes at different weight fractions to examine the sintering behaviors, production parameters, colors, surface properties and antibacterial properties. It was shown that modified MicNo® was very effective against bacteria even at relatively low concentrations due to its designed morphology and high surface covering ability.

Keywords: Sanitaryware, MicNo, Antibacterial Surface

111 - ABS 754

TILES SURFACE WEAR RESISTANCE: INFLUENCE OF THE GLAZE COMPOSITION

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The demand of decorated porcelainized ceramic floor tiles with high surface wear resistance, consistent with the maximum level U4 advocated in Mazaud test under the UPEC classification, is increasing. At the same time, aesthetic and visual changes of the material must be minimized, so that solutions can cover very broad chromatic and aesthetic ranges.

In order to try to achieve these goals, the influence of mullite addition (0, 4, 7 and 10 wt.%) to a transparent porcelain stoneware glaze on the surface wear resistance of porcelainized ceramic floor tiles was studied. After mechanical homogenization, the mullite-reinforced glazes were applied by jet spraying, as a final coating, over unfired tiles with a layer of industrially applied engobe. The pieces were dried and then fired in a semi-industrial gas kiln with a cycle that simulates the industrial one.

The surface abrasion resistance of the fired ceramic tiles was first evaluated by the PEI method according to ISO 10545-7 standard. Then, the samples that exhibited a better performance in the PEI test were industrially prepared and subjected to the Mazaud test according to Cashier CSTB 3778_V3 – 2018 and the obtained results were correlated to the glazes composition.

Commercial mullite powder was characterized by means of XRD, SEM/EDS and Coulter. The mullite reinforced glazes were characterized by XRD, SEM/EDS, DA, DTA/TG and their colour was evaluated by measuring the CIEL*a*b* coordinates.

Keywords: Glaze, Wear resistance, Mullite

112 - ABS 187

EFFECT OF Li_2O ON DIELECTRIC, OPTICAL AND STRUCTURAL PROPERTIES OF YTTRIUM BOROSILICATE GLASSES

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Composition 55SiO2-30B2O3-xLi2O-(15-x)Y2O3 (x= 00, 05, 10, 15) are synthesized using melt- quench technique. All as-prepared samples are sintered at 800°C. As the concentration of lithium increases, density and molar weight of the samples decreases. The structural, optical and dielectric properties of the sintered samples are characterized using X-ray diffraction, FTIR, UV-visible and impedance analyzer. XRD spectra show the crystalline nature of the sintered samples. Optical band gap of the samples lies in insulator range. Lowest optical band gap is observed for YL-10 sample i.e., 3.04eV. Only YL-10 sample shows maximum change in the dielectric constant at various frequencies.

Keywords: Glasses, optical, dielectric

113 - ABS 236

INNOVATIVE FULL-BODY DECORATED CERAMIC SLABS OBTAINED BY A CIRCULAR ECONOMY PRINCIPLES ORIENTED PROCESS

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Aim of this work is to show the results obtained in the framework of the European project LIFE15 ENV/IT/000369 titled "New model of circular economy that also predisposes the use of waste materials in other industries" whose acronym is ECLAT and the main objective of which consists in applying and validating the principles of a circular economy approach to the manufacturing of ceramic slabs reproducing the characteristics of natural stones to be employed in kitchen tops, bathroom countertops without the use of digital decoration technology.

Particularly, in order to pursue the circular economy principles, a composition of ceramic body containing up to 40 wt. % of waste material was first selected. The atomised mixtures were then formed and decorated (employing further waste materials) through a plant comprising a loading station (where the powders are properly deposited on a belt) and a decorating one designed in order to allow the full body decoration. The subsequent dry cutting operations allowed all the generated wastes to be subsequently reintroduced in the industrial cycle. The formed slabs were then subjected to thermal process in order to obtain the final product of 163x324 cm2 and 2 cm of thickness.

In order to prove the environmental sustainability characteristics of the here presented innovative product, obtained by exploiting a circular economy principles oriented process, the Life Cycle Assessment (LCA) methodology (from the "cradle to the grave") was applied to quantify in an objective and trustworthy manner its potential environmental and socio-economic impacts and compare them with those characterizing a more traditional ceramic slab. The LCA study was carried out according to ISO 14040 and ISO 14044, and by using the SimaPro 8.3 software and the modified IMPACT 2002+ v2.10 evaluation method.

Keywords: circular economy, ceramic slabs, life cycle assessment

114 - ABS 169

FABRICATION AND CHARACTERIZATION OF SILICATE BASED GLASS FOAMS AS BUILDING INSULATION MATERIALS

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Due to the limited energy resources, “energy saving” has become a prominent subject. In recent years, organic thermal insulation materials have widely used thanks to their great favor to energy saving. However, these organics are flammable and to find alternative materials, many researches have been carried out with the inorganic materials. In this study, silicate based glass foams were produced and effect of MgO, CaO, BaO, B2O3 and Al2O3 addition and different sintering temperature/time on physical and chemical properties of the foams were investigated. Structural and microstructural analysis were performed via XRD, SEM, FTIR and BET techniques. According to the obtained relatively low thermal conductivity (in the range of 40-50 mW/mK), silicate based glass foams can be considered as promising insulation material.

Keywords: Thermal insulation, glass foam, Silicate

115 - ABS 170

HIGH TEMPERATURE BEHAVIOR OF ANDALUSITE, SILIMANITE AND ZrO_2 MIXTURES

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Andalusite and sillimanite are polymorphic forms of anhydrous aluminum silicate. Their general formula can be written as Al2SiO5. The distinction between this polymorphic forms is due to the different coordination of the Al3 + in these compounds (coordination number: 4 - sillimanite, 5 - andalusite). During heating andalusite and sillimanite convert into mullite. In the SiO2-Al2O3-ZrO2 ternary system, mullite coexists with zircon (ZrSiO4). Therefore, they can be used in a mullite-zirconia refractories production. This work focused on the detailed study of andalusite and sillimanite into mullite and zircon (ZrSiO4) transformation.

Raw materials used in preparing the samples were commercial andalusite (Al2O3: 53.8 wt %; SiO2: 43.1 wt. %), sillimanite (Al2O3: 60.4 wt %; SiO2: 37.3 wt. %) and ZrO2 (chemically pure analytical reagent). Different amount of ZrO2 was added. The mixtures were fired up to 1500°C.

Phase composition and microstructure of the fired samples were identified by XRD and SEM/EDS, respectively. The linear change, apparent density, and open porosity were also tested.

Regardless of whether it was andalusite or sillimanite, the amount of formed ZrSiO4 was similar. In the analyzed mixtures, significant differences in the formation of mullite were found. At the maximum tested temperature, mullite and zircon were formed in the andalusite mixtures. No complete mullite transformation occurred in mixtures with sillimanite, significant amounts of sillimanite were identified.

The work was partially supported by statutory founds of Faculty of Material Science and Ceramics, AGH University of Science and Technology, Krakow, Poland

Keywords: andalusite, sillimanite, zirconia

116 - ABS 938

DETERMINATION OF SUSPENSION REDISPERSION QUALITY WITH STATIC MULTIPLE LIGHT SCATTERING

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A technique based on Static Multiple Light Scattering is proposed to characterize dispersions all along their formulation process from dispersibility to redispersion passing by physical stability. The formulation of suspensions considers the conditions to prepare an homogeneous suspension and keeping it stable as long as possible. Depending on the application, the suspension can settle and need to be redispersed before use. The formulation department needs to control the redispersion process to advice consumer the conditions to apply to reach good dispersibility level.

The technique presented here has the advantage to measure the suspension in a large range of concentration between 0.0001 and 95%, for sizes between 10 nm and 100 µm without sample dilution.

In this work we present different studies showing how the technique is useful in the different steps of the formulation like dispersibility characterization of pigment, mean size measurement, suspension characterization after redispersion under different stress.

117 - ABS 105

THE DESULPHURIZATION OF BALIKESIR – DÜVERTEPE KAOLIN BY FLOTATION TO BE USED IN CERAMIC INDUSTRY

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Kaolin is an essential raw material for ceramic industry. However, the impurities in kaolin such as SO3, prevent the direct use of it in production because of the cracks and pores occurred at elevated temperatures. Kaolin is the most important and crucial input in the ceramics industry hence, the failure induced by the impurities in the raw materials can be costly. The objective of this study is to investigate removing SO3 bearing alunite mineral from Balikesir – Düvertepe region kaolins in Turkey by flotation method and utilize the enriched kaolin in ceramic tile industry. The effect of particle size, solids content and the flotation scheme were the parameters studied. As a result of the flotation studies, SO3 content of the kaolin decreased from 2.34% to 0.52% which renders its use possible in ceramic bodies. Furthermore, firing tests were carried out on treated kaolin and properties such as shrinkage (%), water absorption (%), colour features expressed as L, a, and b were measured. Results of the tests revealed that the enriched kaolin may replace low SO3 content imported kaolins used in ceramic tile bodies.

Keywords: ceramic tile, kaolin enrichment, flotation

118 - ABS 91

NEW GEOPOLYMERS AS INNOVATIVE PRODUCTS FOR TILE INDUSTRY

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Objective: The aim of this project is to develop energy saving methods for manufacturing tiles by using geopolymerization as an innovative processing technique. Ceramic tiles are usually produced by sintering at temperatures ranging between 1100-1250 °C as function of natural raw materials selected in the mixture. Geopolymers are amorphous aluminosilicate inorganic polymers obtained by mixing alkali-silicate solutions with reactive aluminosilicate precursors. Geopolymerization may occur at room temperature or at temperature lower than 100 °C and different type of waste may be used as geopolymer precursors. The possibility to obtain geopolymer tiles with properties comparable with those exhibited by traditional tiles is extremely challenging as geopolymerization would represent a huge energy-saving in the consolidation process as well as in natural raw materials exploitation.

Materials & Methods: The research started with an accurate physico-chemical characterization of wastes produced during the ceramic cycle. Granulometry studies were carried out to reach an optimized grain size distribution of the investigated precursors. Initially several innovative mix designs were tested in order to determine the waste capability to be alkali-activated. Casting and pressing methods were used for shaping and different curing conditions were tested to optimize the process and the geopolymer properties. Thermal characterization by DTA-TG analysis, optical dilatometer and heating microscope as well as microstructure analyses with XRD and SEM techniques have been carried out on final products.

Results: The synthetized geopolymer tiles exhibit interesting properties comparable with those usually shown by BIb ceramic tiles. In particular, the geopolymer tiles exhibited a water absorption less than 1.5% and a mechanical strength more than 22 N/mm2. Results show that the dry rectifying powder, activated by potassium hydroxide and K-silicate reactants, are the most promising reagents to develop the best geopolymer, minimizing water absorption and maximizing mechanical strength of the hardened product. The macro-porosity of the pressed geopolymers is lower than the casted samples where air remains trapped in the hardened mix. The geopolymers thermal characteristics are very different compared to those shown by ceramic tiles, as a very pronounced thermal expansion occurs over 500 °C, thus preventing decoration with firing.

Conclusions: The geopolymerization approach can be used to obtain tiles according to the requirements reported in ISO 13006. However decoration process shall still be faced. The obtained geopolymer tiles can be considered potentially appealing for floor and wall covering applications, but an improvement is necessary if technological features comparable to porcelain tiles (BIa) are desired.

Keywords: Flooring geopolymers, Geopolymer tiles, Geopolymerization

119 - ABS 49

THE EFFECT OF GRANULATION OF DOLOMITE ADDITIVES TO CERAMIC CLAY ON THE COLOR AND PROPERTIES OF FIRED CERAMIC MATERIALS

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The aim of this work was to investigate the effect of granulation of dolomite additives to ceramic masses based on cream firing Borkowice clay on the color and properties of fired ceramic materials.

The work was divided into two stages: I - analysis of raw materials and II - characteristic of ceramic materials. In the first stage, the following tests were carried out: granulometric analysis, color analysis (L*a*b color coordinates, Whiteness index, Yellowness index) and chemical composition. In the second stage, the following tests of ceramic materials obtained in two different firing temperatures were carried out: color analysis (L*a*b color coordinates, Whiteness index, Yellowness index), flexural strength, compressive strength, water absorption, open porosity and apparent density. Moreover the results of microstructure and phase composition tests for selected ceramic materials were presented.

After carrying out these analyses it was noticed that the different granulation of dolomite additives to ceramic clay causes differences in the properties of fired ceramic materials.

Keywords: granulation, mineral additives, color

POSTER SESSION 3

1 - ABS 750

PRELIMINARY DATA ABOUT TILES FROM S. MARCO HILL IN PATERNÒ (CATANIA- SICILY)

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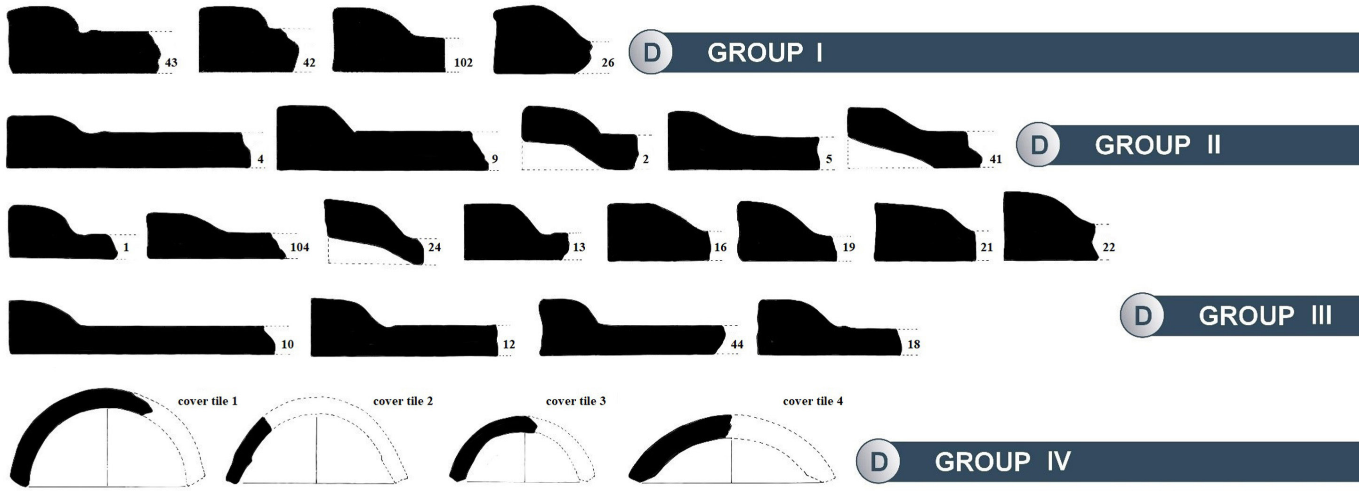
San Marco hill, on the outskirts of Paternò, is far 2 kilometres from Simeto river and is characterized, in the upper part, by the presence of mud volcanoes named Salinelle, which produce gas and hot water. Easy access to water helped human settlement since Neolithic with a millenary continuity. Archaeological excavations started in 1994 allowed to identify a Late Neolithic village and several finds datables between the Copper and the Late Bronze Age. In June 2016, two sides of the hill were investigated. On the southwest side, the excavation, after an illegal dig and two surveis in the surrounding area, allowed to recover materials related to a long dated human attendance dating from the Early Bronze Age to the Hellenistic-Roman period. Among finds there is a considerable amount of flat tiles in different forms, belonging to a necropolis with “cappuccina” tombs as well as to a small sacred building, destroyed in an unspecified period. The northern side of the hill is affected by the presence of structures, dating between the first and the second century A.D. and for a long time probably identified as a thermal building because of the fragments of circular bricks used in the construction of pilae. The investigations in previously unexplored rooms have revealed a tick layer of semi-circular tiles belonging to a storage deposit. The study of these materials, too often excluded from old scientific publications or simply left on the field after archaeological excavations, have allowed to express important hypotheses about the times and ways of human attendance of San Marco hill. It has been possible to hypothesize the presence of a very important sacred area and a necropolis in the Hellenistic age and finally, a structure of craftmade or rural type in Roman period, thus definitively rejecting the presence of the baths. The objective of the study is to attempt a chrono-typological series of such artefacts, based on the very few examples published in other papers: they have been subdivided according to the shape and the rough estimate of the proportions of each find. The autoptic analysis conducted on these building elements also wants to deepen knowledge about the raw materials used for clay pastes, in relation to the presence of supplying sources scattered throughout the territory. This preliminary study, combined with laboratory analysis, will help to know also the cooking temperature of artifacts and possible degreasings used in addition to the lava crumbs, available in Etnean area. Moreover, clear traces of work defects, visibles especially on the Roman tiles, can allow us to exclude, in this moment, the hypothesis that these building elements were not imported from another production center, but realized in a local kiln, which has to be identified in the surrounding area.

Keywords: tiles, excavations, ceramic



2 - ABS 678

ELECTROCHEMICAL SCREENING OF INKA POTTERY OF DIFFERENT PERIODS FROM THE QOTAKALLI ARCHAEOLOGICAL SITE IN THE AREA OF CUSCO (PERÚ)

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Objectives: To develop a novel method for screening archaeological pottery regarding provenance and age based on solid state electrochemistry techniques. Application to a set of samples from the archaeological site of Qotakalli near Cusco (Perú) covering since the Initial to Colonial periods.

Materials And Methods: The voltammetry of immobilized microparticles (VIMP) methodology was applied to pottery samples at the submicrogram level extracted from cross-sections of fragments of aríbalos, cuencos, jars and plates. Sample modified graphite electrodes were put into contact with 0.10 M H2SO4 and the voltammetric response upon application of different potential inputs was recorded.

Results: VIMP responses consisted of cathodic signals for the reduction of Fe(III) minerals, hematite with different degrees of hydration and crystallinity, in particular, and anodic signals for the oxidation of Fe(II) ones, accompanied by electrocatalytic signals on the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). The obtained voltammetric profiles permitted to discriminate between samples of different colors and periods using several peak current ratios which define tendency curves allowing for the screening of pottery samples.

Conclusions: VIMP provides a sensitive method for characterizing pottery samples only requiring amounts at the nanogram level. Tendency graphs based on electrochemical data permits to separate pottery fragments corresponding to different manufacturing techniques and historical periods. Acknowledgements: R+D project CTQ2017-85317-C2-1-P, MINECO/AEI/FEDER, UE.

Keywords: voltammetry of microparticles, pottery, inka culture

3 - ABS 548

STAINED GLASS CERAMIC JEWELRY AND ART BY CERAMIC STEREOLITHOGRAPHY

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In this paper, the stained glass ceramic hyperfine complex structure has been implemented. We prepared the specialized glass slurry, and printed the green parts from the high precision ceramic stereolithography apparatus, after debinding and high-temperature sintering, the glass ceramic parts could be acquired that the minimum structure is down to 0.1 mm, have very good surface roughness and density. This method can implement any traditional art ceramics, including glass, purple sand, ceramic minerals around the world, and add glass ceramic color agent flexible, we can also realize surface polishing after sintering. We have achieved high precision of jewelry, sculpture, and many artworks, etc. And it will be used to the new artwork and antique restoration.

Keywords: Stained glass ceramic, Stereolithography of ceramic, Jewelry and art

4 - ABS 495

FORMULATION OF GLASS-CERAMIC INK FOR DIGITAL INK-JET PRINTING

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Ink-jet printing technology is very attractive due to its capability of direct and fine printing onto various objects. Recent studies have been focused on the expansion of the ink-jet printing application from general consumer and design company use to various industrial fields, ranging from prototype production to parts manufacturing. Especially, the use of ink-jet printing technology for decoration of tableware, tiles, and other ceramic products has many advantages such as fast process, high efficiency, low cost and customized manufacturing. For the application of ink-jet printing technology to ceramic product decoration, ink with highly dispersed inorganic pigment is required. Here we report the formulation and printability of glass-ceramic complex ink for ink-jet printing. Inorganic pigment and frit were atomized to improve dispersion stability. Glass-ceramic ink was formulated using aqueous solution to minimize VOCs evolution. Viscosity and surface tension were optimized for a suitable jetting from printhead, and the printability on various substrate was investigated in detail.

Keywords: Ink-jet printing, Ceramic ink, Pigment

5 - ABS 463

MICROSTRUCTURE AND FORMATION MECHANISM OF GOLD-COLORED JAPANESE BIZEN STONEWARE

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The microstructure and formation process of gold-colored pattern on traditional Japanese unglazed stoneware called Bizen was studied through model experiments. The gold-colored surface appeared where the shaped clay was in contact with straw. The clay containing approximately 2-3 wt% Fe_2O_3 and rice straw was fired in a climbing kiln with red pine wood used as fuel. Firing in a strongly reducing atmosphere generated by burning fuel is essential for lustrous coloring; therefore, it is reasonable to assign the luster to optical interference within carbon films deposited on the stoneware surface. Through transmission electron microscopic observations, we found the formation of thin Al-substituted hematite (α-$Fe_{1.9}Al_{0.1}O_3$) layer with approximately 100 nm in thickness on the stoneware surface instead of carbon film.[1]

We also succeeded in reproducing the gold-colored pattern on model sample surfaces by controlling oxygen partial pressure during the heat treatments in an electric furnace. Bizen clay pellets were heated in an alumina crucible to 1230 °C in air with laterally surrounding the pellets with powdered potassium carbonate that was used instead of rice straw. The atmosphere was then switched to a strongly reducing mixed gas of 10 vol% CO and 90 vol% Ar, in which the pellets were held at the same temperature for 6 h and subsequently cooled to 900 °C. The atmosphere was then switched back to oxidizing and the pellets were held at this temperature for 2 h followed by cooling to room temperature. The sample surface obtained in this process appeared luster gold color and had Al-substituted hematite with approximately 100 nm in thickness.

It was concluded that the gold-colored pattern was caused by the yellowish color from thin Al-substituted hematite layer and reflected light from the glassy phase formed on the surface.

[1] Y.Kusano, M.Fukuhara, T.Fujino, T.Fujii, J.Takada, M.Takano, Cryst. Growth Des., 18, 4017,2018.

Keywords: Unglazed Ceramic, Bizen Stoneware, Microstructure

6 - ABS 459

THE FIRST ARCHAEOMETRIC CHARACTERIZATION OF DECORATED POTTERY FROM THE ARCHAEOLOGICAL SITE OF VILLA DEI QUINTILI (ROME, ITALY)

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This work focused on the study of decorated pottery dated back to XVI century from the Roman archaeological site of Villa dei Quintili, a monumental complex located in the south-eastern part of Rome (Italy). An archaeometric study was undertaken to analyse five archaeological samples in order to define textural features and raw materials used for their production, along with the chemical-physical composition of the superficial decorative glazed coatings. For this purpose, different analytical methods were used, such as polarizing optical microscope (POM), X-ray diffraction (XRD), micro-Raman spectroscopy, X-Ray fluorescence (XRF) and electron microprobe analysis coupled with energy dispersive spectrometry (EMPA-EDS). The results of such a multidisciplinary approach allowed us to achieve important results crucial to recognize the shards as majolica of the Renaissance period, improving knowledge about manufacturing processes of these renowned painted ceramic artefacts.

Keywords: decorative glazed coatings, pottery, EMPA-EDS

7 - ABS 325

MEDIEVAL AND POST-MEDIEVAL ESCAVATION POTTERY IN THE NATIONAL MUSEUM OF RAVENNA. A DIFFICULT RECONSTRUCTION OF AN UNKNOWN HERITAGE

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Objective The National Museum of Ravenna preserves an important amount of pottery coming from the excavations that took place mainly in the city center of Ravenna from the second half of the 19th century. This is a very interesting material that can provide meaningful information. However, due to numerous problems that occurred in the early years of the 20th century, the origin of most of those materials is unknown. For some time, I have undertaken a patient research work in order to assort with greater accuracy all the material depending on the contexts of origin. My effort is aimed to report about the new information and data developed by this research.

Material and Method The pottery, both without coating or glazed, is dated from the 14th to the 17th century,. All the illustrated material will be related to the finding location and to the morphological, typological and chronological features.

Results This survey allowed to associate with certainty some of the pottery currently kept in the Museum to at least 5 contexts and to accurately identify all the data concerning the discovery, generally occurred between the end of the 19th and the first decades of the 20th century. The results overtake the traditional out-to-date information of the place of origin reported by the inventory and provides a more detailed illustration of the stored material. The contexts that were studied are specifically: the furnace for ceramics near the church of S. Giorgio dei Portici, the cloister of Classe in Città, the cloister of San Vitale, the cloister of Porto in Città and the Archbishopric.

Conclusions This research allows to increase the knowledge concerning the production and use of ceramics in medieval Ravenna, a topic that still needs to be gutted in its entirety.

Keywords: Medieval pottery, Glazed pottery, Ravenna

8 - ABS 304

IMPROVEMENT OF DESIGN OF CERAMIC PRODUCTS WITH WATER PAINT SOLUTIONS IN THE PAINT COMPOSITION

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Used the water paint solutions that can improve the decorative properties of coatings in ceramic. Considered the mechanism of their action in water paints.
1.actualness and goal of researching
Directed changing of acid-base properties of surface such as in vanish-paint compositions for decoration of ceramic tile, various types of ceramic goods is one of the important problems of physical and colloidal chemistry and chemistry of solid.
To create multi-color décor andreplace underglaze decal with silk-screen printing the present studies were carry out.
2. main part
Underglaze paint water solutions are saturated hydrochloric and sulfate salts of some metals forming during firing paint oxides or metal silicates . Main nomination of underglaze paint solutions is creating a specific halo effect around the outline of the picture using carbamide-formaldehyde oligomers in vanish-paint vaterial (these oligomers don.t allow penetrating of the
paintsolutionthrough the thickness of the faience sample), various paint tones with special contour charm and shine of glaze. Use of paint solutions without expensive ceramic pigments is also cost-effective[1].
It was found that selected combination of the mixture of fillers(chalk and dry porcelain) and the smallest quantity of pigment allows to get a specific decorative effect as tone up, softening and changing the color tone and to create the sault halo around the outline of the picture
The following tasks have been achieved there by: preparation of paint pastes for known material with carbamide-formaldehyde oligomers(with adding hydrochloric salts Co, Ni, Cu), apply the paint composition with silk-screen printing and to research physic-chemical and decorative properties of paint coatings on the ceramic surfaces.
The decorative properties of paint coatings were analyzed using the methods according to specifications for faience ware(54395-2011): 1.leveling property of glaze after firing was determined visually(quality of surface); 2. clearness of picture outlines(mm) was determined as paint spreading beyond the picture outline; 3. indefined picture outlines (the distinctive effect)were determined with the size of sault halo around the picture outline,(mm)(visually); 4. brightness of tone,presence of semitones (visually).
It were studied technological properties of paint:
1.the time of impregnation and drying to touch,mm;
2.separating of pigment and plastic binder on the surface(visually). 3.multiplicity of drawing
3.conclusion
It is found that can create multi-color décor using selected combination of the fillers' mixture and water paint solutions of some metals in paint composition. Thus, developed compositions can be used for highly artistic design.

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Keywords: design, vanish paint material, decorative properties

9 - ABS 276

INTEGRATED ANALYTICAL TECHNIQUES ON A PAINTED TERRACOTTA BY LUCA DELLA ROBBIA

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The Madonna with Child placed in the Sacresty of the Florentine Church of Santa Felicita is a beautiful example of polychrome painted terracotta of the first half of the 15th Century in Florence. Attributed to Luca della Robbia by art historians, it was probably made around 1430, before he started to work with his famous glazed terracottas. This paper shows the results of the scientific analyses carried out on this sculpture (fig. 1), with the aim to study the composition of the terracotta support and painting materials, original and not. It is believed that the sculpture has undergone some change in colour after the restoration occurred a few years ago, so restoration materials were also examined. On first, imaging exams like visible light photograph, IR reflectography and false colour IR were carried out. Reflectance spectrometry in the visible range (vis-RS), colorimetry (CM) and energy-dispersive X-ray fluorescence spectroscopy (ED-XRF) were performed in order to gather as much information as possible on the work, reducing the sampling to the most important areas to be studied. As a second step, a set of micro-fragments was analysed by optical microscopy (OM), X-ray diffractometry (XRD), environmental scanning electron microscopy with energy dispersive spectroscopy (ESEM/EDS). Raman and FTIR spectroscopy. The collected data allowed to characterize also the variety of non-original compounds, depending on the many restorations the statue underwent during centuries, as typical of painted sculpture. In fact, for example, the Virgin’s cloak is all repainted with Prussian blue, probably more than one century ago, perhaps because damaged. About technique, a white ground containing lead white mixed with linseed oil was applied over the red terracotta and before the simple coloured layers, that contain vermillion, red ochre, a coccid-based red lake, lead white, indigo, azurite, also painted with an oil medium.

Keywords: painted terracotta, Luca della Robbia, non-invasive + micro invasive

10 - ABS 192

PERLITIC REDUCTION GLAZES COLORED BY COPPER(II) OXIDE

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This study aims to use expanded perlite as a raw material in reduction glazes.

Perlite is an amorphous volcanic glass which it's chemical composition mainly includes 65-78% SiO2, 8% alkali oxides and 2-5% molecular water by weight and other oxides.

Perlite can easily be supplied commercially. Perlite has some physical and chemical advantages. One of them, it can easily be grinded when it is expanded. In this way, the problem of grinding in the preparation of glaze batches is reduced.

Different glaze recipes were prepared by using (Perlite-Ulexite and Orthoclase). 1 and 3 % (by weight) copper (II) oxide was used as a coloring agent. The batches were prepared by wet grinding technique.
The prepared glazes were applied to the test plates of chamotte body by pouring method. Samples were fired at 910°C in oxidation atmosphere. Reduction firing is performed in the same kiln at 730°C. Results were discussed and the selected glazes were applied to different forms.

Finally, different colored glazes changing from metallic copper and opaque red to blue color shades were obtained.

Keywords: perlite, reduction glazes, artistic ceramic glazes

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