

PREPARATION OF ZIRCONIUM TITANATE CERAMICS BY SOL-GEL PROCESS

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Abstract: Zirconium titanate, ZrTiO_4 , was synthesized by sol-gel method from zirconium butoxide and titanium isopropoxide. ZrTiO_4 gel was dried to obtain amorphous powder, which was ground to under 80 μm , calcined at 500 °C and milled to homogenise size distribution of the powder. Differential scanning calorimetry indicated crystallization of ZrTiO_4 at ~700 °C, which was confirmed by X-ray diffraction analysis. To study the influence of temperature on crystallization of ZrTiO_4 , milled powder was also sintered at 900, 1100, 1200, 1300 and 1400 °C for 8 hours. It was found that crystallite size, as determined by Scherrer equation, increases with increasing temperature of sintering. Change of cell parameters indicates unusual transformation from disordered to ordered structure with increasing temperature. Applicability of ZrTiO_4 sols for preparation of thin coatings on glass substrates was also investigated. Increasing thickness of coatings leads to cracking of the coating, which can be prevented by decreasing sol viscosity or the speed of drawing the substrate from the sol.

Key words: crystallization, sol-gel process, thin coatings, zirconium titanate

Ključne riječi: kristalizacija, sol-gel postupak, tanke prevlake, cirkonijev titanat

1. INTRODUCTION

Zirconium titanate, ZrTiO_4 , is a ceramic material with very good thermal and electrical properties and high resistance to heat and corrosive environment. This lead to its widespread use in electronic components for telecommunication purposes, such as condensers and resonators [1]. Zirconium titanate is also used for catalysts [2,3], and lately its applicability for humidity sensors is also being investigated [4]. High purity and homogeneity of ceramic material is essential for all these applications. This is difficult to achieve by classical procedure that consists of sintering a stoichiometric mixture of zirconia (ZrO_2) and titania (TiO_2) powder at temperatures up to 1600 °C for several days [1]. High-energy milling of ZrO_2 and TiO_2 , which reduces crystallite size to give almost amorphous powders, can lower the transition temperature as low as 1100 °C. But this approach is also energy costly, and attrition of milling balls can increase content of impurities [5]. Because of this, sol-gel process is increasingly used to prepare homogeneous and amorphous ZrTiO_4 powder that crystallizes at temperatures several hundred degrees lower than in previously described methods. ZrTiO_4 can be prepared by hydrolysis and condensation of inorganic salts [3] or alkoxides [2]. Ceramics synthesized by sol-gel process are very pure, their microstructure is comparatively easy to tailor, and the process is also suitable for preparation of thin films [6]. In this work we investigated influence of sintering temperature on crystallization of ZrTiO_4 prepared by sol-gel process, and determined the best conditions for drawing thin ZrTiO_4 films on glass substrates.

2. EXPERIMENTAL

Zirconium titanate, ZrTiO_4 , was synthesized by sol-gel method from zirconium butoxide ($\text{Zr}(\text{C}_4\text{H}_9\text{O})_4$, 80 %, Fluka) and titanium isopropoxide ($\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$, 97 %, Aldrich), stabilised with 0.3 mol of acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$, Fluka) per mole of alkoxide, in 2-propanol solution. Stabilised alkoxides were hydrolysed with stoichiometric amount of water for full condensation of alkoxides (2 moles per mole of alkoxide), added as 4.64 mol/dm³ nitric acid that served as catalyst. Transparent sol was left to gel at room temperature. The resulting gel was dried at 110 °C, ground and sieved to remove particles larger than 80 µm, calcined at 500 °C to remove residual organic content, and milled. Milling was performed for 2 hours in air using a planetary ball mill Fritsch Pulverisette 6 with vial and balls of 94 % zirconia, with rotation speed of 500 rpm and powder-to-ball weight ratio of 1:10.

Table 1: Composition of sols used for preparation of amorphous ZrTiO_4 powder (sol A) and for drawing the thin films (sols A and B)

	Sol A	Sol B
Zr-butoxide	1 mol	1 mol
Ti-isopropoxide	1 mol	1 mol
acetylacetone	0.6 mol	0.6 mol
nitric acid	0.4 mol	0.4 mol
water	4 mol	4 mol
2-propanol	15 mol	30 mol

Thermal behaviour of the milled powder was studied by simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) on a Netzsch thermoanalyzer STA 409. Sample was heated from room temperature to

1350 °C at a heating rate of 10 °C/min in a synthetic air flow of 30 cm³/min. Milled powder was sintered for 8 hours in a muffle furnace with Pt-PtRh thermocouple at 900, 1100, 1200, 1300 and 1400 °C. Furnace was heated to sintering temperature at 23 °C/min. X-ray powder diffraction (XRD) analysis was performed on Phillips PW 1820 instrument making use of CuK α radiation with a scanning rate of 0.12°/min. Crystallite size was determined using Scherrer equation, while crystal lattice parameters were determined from positions of diffraction maxima by computer program *Unitcell* [7]. Fully crystallized rutile, TiO₂, was used as a standard both for crystallite size and for position of diffraction maxima. Preparation and characterization of ZrTiO₄ powder is schematically shown in Figure 1.

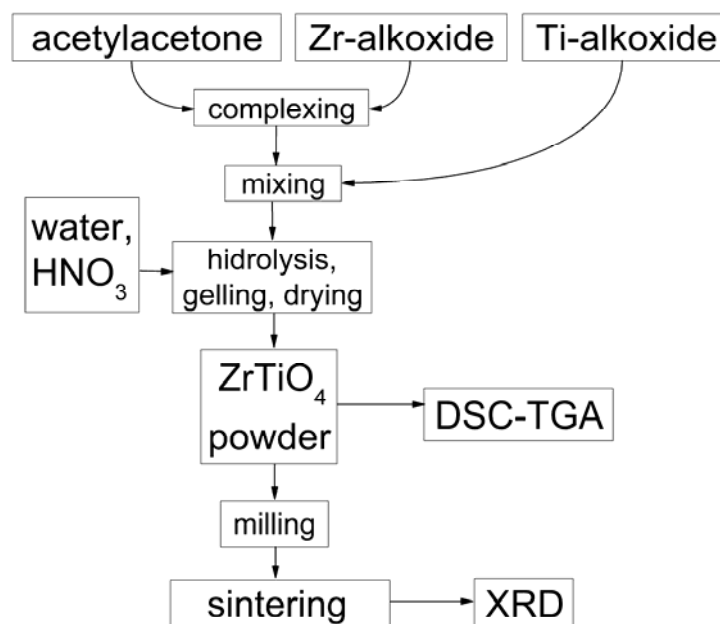


Figure 1 – Schematic representation of preparation procedure and characterisation of ZrTiO₄ powder

Thin ZrTiO₄ films were drawn on glass microscope slides previously cleaned with acetone, making use of custom-made dip-coating apparatus with drawing speeds of 0.18 and 0.05 cm/s. Viscosity of sols was modified by dilution of sol with 2-propanol, from 8.4 mPa s (sol A) to 3.3 mPa s (sol B), as determined by Höppler viscosimeter at the constant temperature of 20 °C. Viscosity of the sols increased due to condensation proceeding during 3 hours of drawing to 91.8 mPa s and 38.4 mPa s, respectively. After drawing, coatings were dried at 110 °C for one hour, and each slide was coated from 1 to 3 times. Morphology of coatings was investigated by MOTIC BA200 optical microscope.

3. DISCUSSION OF RESULTS

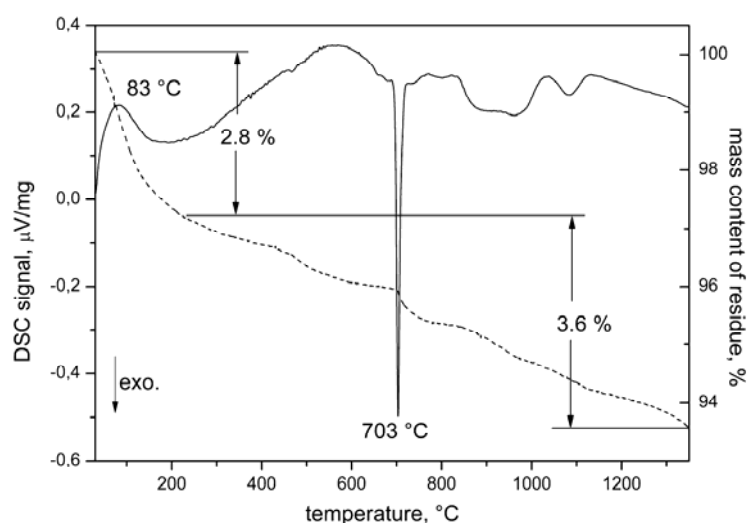


Figure 2 – Combined differential scanning calorimetry and thermogravimetric analysis of ZrTiO_4 amorphous powder calcined at 500 °C, taken in air at 10 °C/min

Results of DSC-TGA analysis are given in Figure 2. The first mass loss evident on the TGA curve and accompanied by a DSC endothermic maximum at 83 °C is due to evaporation of adsorbed water. The mass loss decreases approximately constantly with further temperature increase, which is ascribed to slow degradation of residual organic content. Large DSC exothermic maximum at 703 °C is due to crystallization of amorphous ZrTiO_4 , as confirmed by XRD (Figure 3).

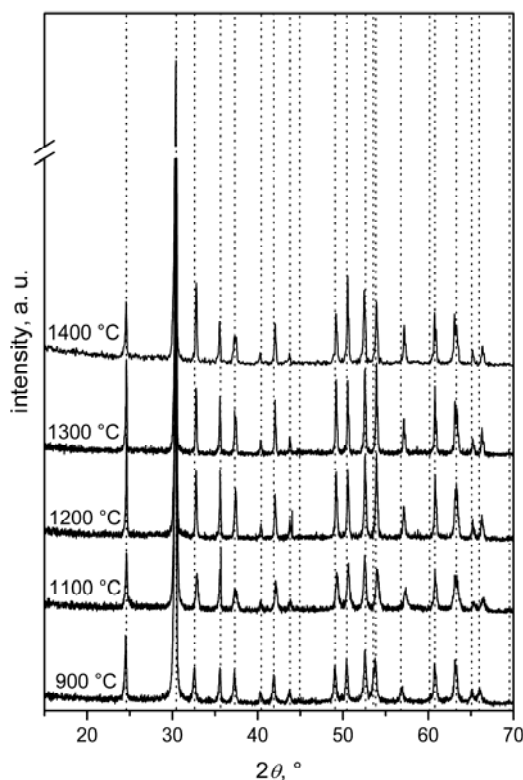


Figure 3 – X-ray diffractograms of ZrTiO_4 powder sintered at denoted temperatures; JCPDS data for zirconium titanate (34-415) shown as dotted lines

Table 2: Crystallite size as determined by Scherrer equation and porosity as determined by mercury intrusion, for ZrTiO₄ powders and tablets sintered at listed temperatures

Temperature, °C	Crystallite size, nm	Lattice parameters, Å		
		<i>a</i>	<i>b</i>	<i>c</i>
900	35	5.036	5.486	4.812
1100	40	5.038	5.440	4.816
1200	90	5.037	5.452	4.810
1300	130	5.034	5.442	4.814
1400	130	5.032	5.436	4.815

All sintered samples are pure crystalline ZrTiO₄, which crystallizes in orthorhombic symmetry. Increase in sintering temperature promotes crystallite growth, which is apparent from decreased width and increased intensity of XRD maxima. Average crystallite size in tablets and unpressed powders was determined from broadening of the XRD maxima by Scherrer equation (Table 2), using TiO₂ sintered at 1200 °C as a standard to correct for the instrumental broadening. The strain contribution to the broadening could be neglected in the calculation at low Bragg angles [8]. The apparent crystallite size expectedly increases with sintering temperature.

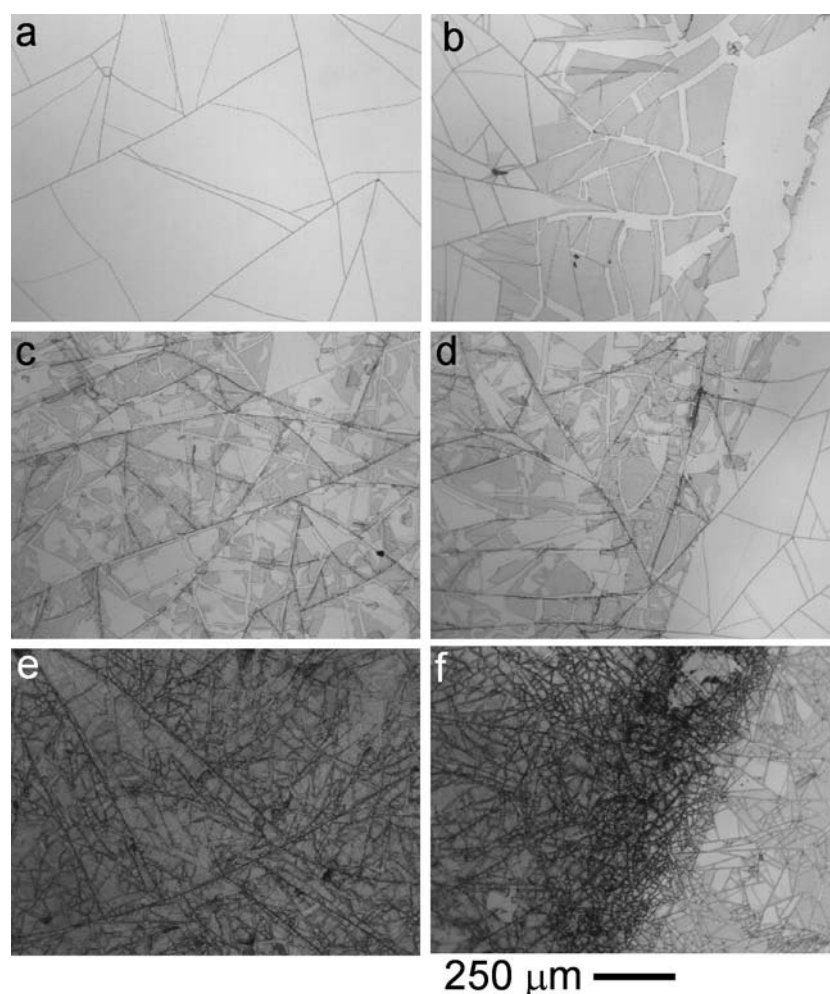


Figure 4 – Morphology of ZrTiO₄ coatings on glass substrate, drawn from sol A with drawing speed of 0.18 cm/s: a, b) one layer, c, d) 2 layers, e, f) 3 layers; b, d, f) edge of coating

Lattice parameter b decreases markedly between 900 and 1100 °C (Table 2), which could be an indication of order-disorder transformation. This is unusual since ordinarily parameter b decreases when disordered high-temperature form changes into more ordered low-temperature form upon very slow cooling. ZrTiO₄ prepared by sol-gel process crystallizes in “high-temperature” disordered state at low temperatures, because the disorder present in the initial amorphous powder is preserved in the crystalline product [9]. The ordering is most probably due to prolonged calcination at higher temperatures [10], but formation of non-stoichiometric ZrTiO₄ or solid solutions is also a possibility [10,11].

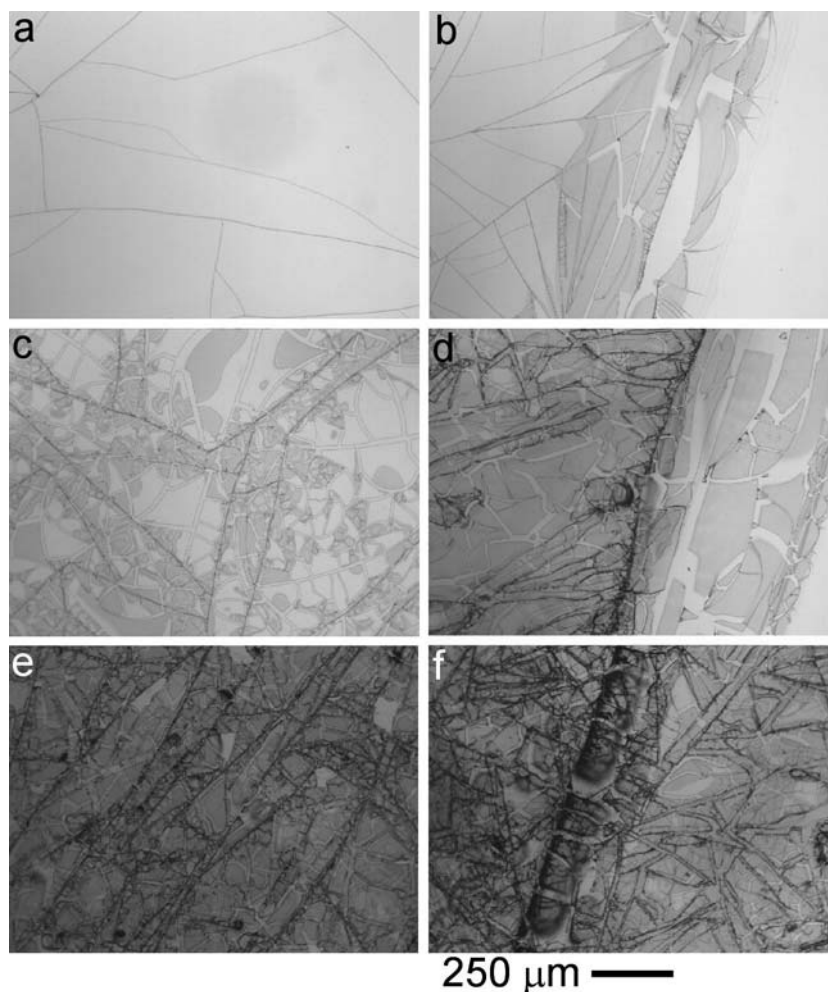


Figure 5 – Morphology of ZrTiO₄ coatings on glass substrate, drawn from sol A with drawing speed of 0.05 cm/s: a, b) one layer, c, d) 2 layers, e, f) 3 layers; b, d, f) edge of coating

Thickness of films depends on viscosity of sols, content of oxides or alkoxides in the sol, temperature and speed of drawing. Too thick films crack upon drying and peel from the substrate, so all of the above mentioned factors have to be optimised in order to achieve crack-free homogeneous films. Morphology of ZrTiO₄ coatings as a result of drawing speed and viscosity/alkoxide concentration of sols are shown in Figures 4-6.

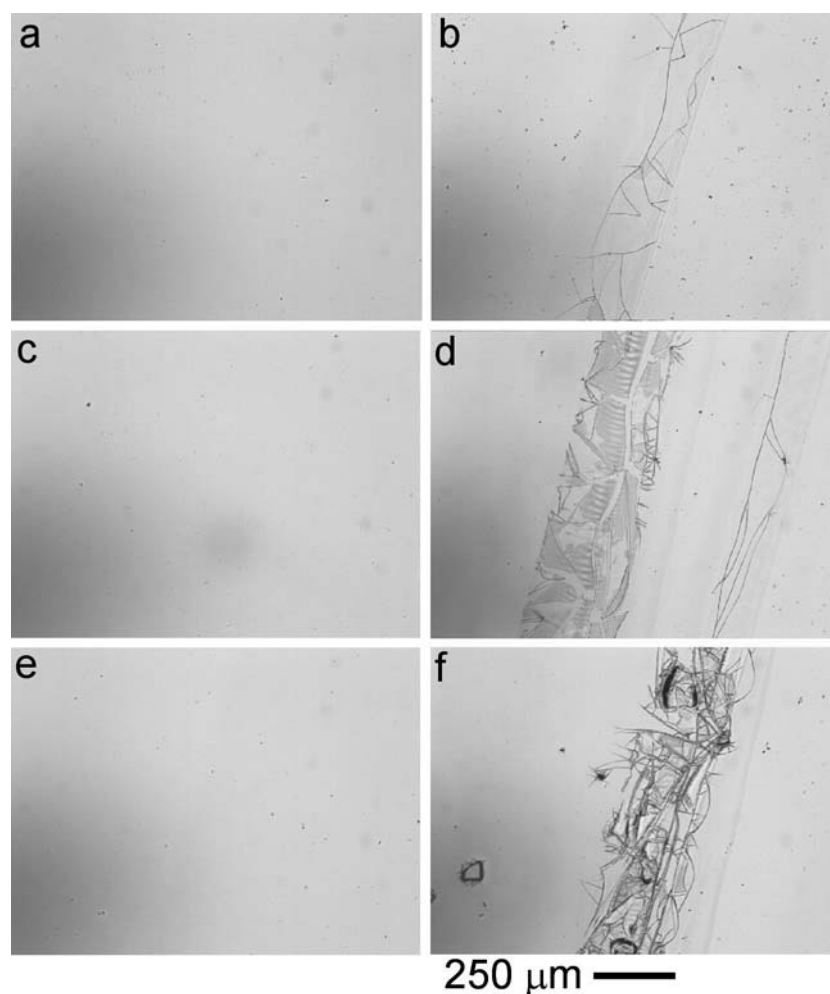


Figure 6 – Morphology of ZrTiO₄ coatings on glass substrate, drawn from sol B with drawing speed of 0.05 cm/s: a, b) one layer, c, d) 2 layers, e, f) 3 layers; b, d, f) edge of coating

Fast drawing speed (Figure 4) results in thick coatings that crack easily, and the cracking is more pronounced in multilayered coatings. Coatings drawn with the slowest drawing speed of the dip-coating apparatus also cracked (Figure 5). Although the cracking was somewhat less pronounced than in previous coatings, there was no practical difference. So, in order to produce crack-free coatings, viscosity and alkoxide content of sols was decreased by diluting with solute. In this manner crack-free coatings were prepared (Figure 6), even after deposition of 3 layers to prepare thicker coatings. Since viscosity increased 10 times during drawing, the decreased alkoxide content in sol was probably the key in producing crack-free coatings. Dilute sol remained stable for over 30 days when stored in tightly closed container.

4. CONCLUSIONS

Stable ZrTiO₄ sols were prepared by sol-gel process from zirconium butoxide and titanium isopropoxide. Powder prepared from the sol crystallizes into orthorhombic ZrTiO₄ in one step at 703 °C. Size of ZrTiO₄ crystallites increases with sintering temperature, while crystalline structure transforms into more ordered form between 900 and 1100 °C. Crack-free coatings were drawn from diluted sol, and thicker coatings could be prepared by depositing several layers.

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