COMMINUTION KINETICS OF PREMULLITE POWDER

KINETIKA MLJEVENJA PREMULITNOG PRAŠKA

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Abstract: Pre-mullite powder has been synthesized by sol-gel process. Differential thermal analysis (DTA) of the powder yielded scan with two exotherms: stronger at ~980°C and weaker at ~1200°C. Using X-ray diffraction (XRD) analysis it has been determined that first exothermic peak is a consequence of Al-Si spinel crystallization, while second peak occurs due to mullite crystallization. The powder was wet milled in planetary ball mill within various time intervals. The particle size distribution of ground samples has been determined using particle size analyzer (PSA). Comminution kinetics of calcined pre-mullite gel is modeled using a classical batch grinding equation based on selection and breakage functions. Analysis of experimental data resulted with model suitable for prediction of particle size distribution of calcined amorphous gel comminuted in planetary ball mill if the duration of grinding is no longer than 128 min.

Keywords: pre-mullite gel, planetary mill, particle size distribution, grinding kinetics.


Ključne riječi: premulitni gel, planetarni mlin, raspodjela veličine čestica, kinetika usitnjavanja.
Introduction

Mullite is a solid solution with a general formula \( \text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x} \) where \( x \) represents the number of oxygen vacancies due to composition-induced substitution of tetrahedral \( \text{Si}^{4+} \) by \( \text{Al}^{3+} \). [1] The high strength at high temperature, low thermal expansion, excellent creep resistance and good chemical and oxidation resistance make mullite an attractive ceramic material for advanced applications [2], for which ultra fine mullite precursor powders are of utmost importance [3]. In order to obtain high-purity mullite precursor powders, sol-gel process is employed [4]. Extensive work has been done related to the processing of sol-gel derived pre-mullite materials, but a complete understanding of all process parameters has not yet been fully achieved.

Traditional approach in comminution modeling is based on population balance models using first order kinetics which requires the determination of breakage and selection functions that are calculated from the batch grinding experiments using particle size range divided into a geometric sequence. The lack of methods for preparing narrow size intervals is often a problem when using population balance method of discretized sizes. Therefore, analytical solution that involves special form of the selection and the breakage functions is useful in kinetic analysis.

The investigation on grinding kinetics of amorphous powders is very scarce and, to the best of our knowledge, grinding kinetics of pre-mullite powders has not been investigated at all. Therefore, this work has been undertaken with aim to provide information about grinding kinetics and particle breakage mechanism of diphasic pre-mullite gel.

Experimental

Aluminum nitrate and tetraethylorthosilicate (TEOS) were used to prepare diphasic mullite gel with alumina/silica molar ratio close to 3/2. The \( \text{Al(NO}_3\text{)}_3 \times 9\text{H}_2\text{O} \) (Kemika) was dissolved in \( \text{H}_2\text{O} \) and TEOS, (Merck) was mixed with ethanol and added dropwise to the nitrate solution. The mixture was stirred under reflux conditions at 60 °C for 8 days. The gel was dried at 110°C and calcined at 700 °C for 4 h to decompose the organics and remove the volatiles. The calcined gel was crushed and ground in a corundum mortar, seized to particles smaller than 63 \( \mu\text{m} \) and stored in a desiccator.

Calcined gel samples were grinded in planetary ball mill Fritsch GmbH, Pulverisette 6 using 250 mL zirconia bowl, and 30 \( \text{ZrO}_2 \) balls of 10 mm diameter with total weight of \( \sim 70 \text{ g} \). 10 g of premullite powder samples, mixed with 10 mL of isopropanol were grinded for 16, 32, 64, 128, 256 and 512 min at revolution speed of 200 rpm. After grinding, the samples were dried at 110°C and calcined at 700°C for 4 h.

The particle size distribution of ground samples has been determined using particle size analyzer Coulter Counter ZM, (Coulter Electronics Ltd., Luton, UK). Samples were dispersed in 1 wt.% NaCl aqueous solution previously filtered to eliminate background count.

The powder samples morphology was investigated with Scanning Electron Microscopy (SEM) TESCAN, VEGA TSS 136LS. Prior to scan, powders were applied to the adhesive graphite tape.

X-ray diffraction analysis (XRD) has been performed on computer controlled diffractometer Philips 1830 with CuK\( \alpha \) radiation. Data were collected between 5 and 70° 2\( \theta \) in a step scan mode with steps of 0.02° and counting time of 2s.

Grinding kinetics is commonly described using population balances. Partial integro-differential equation for size-continuous time-continuous model, assuming well mixed batch process can be written in form [5-8]:

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\[
\frac{\partial^2 D(x,t)}{\partial t \partial x} = -S(x) \frac{\partial D(x,t)}{\partial x} + \int_{y=x}^{x_{\text{max}}} S(y) \frac{\partial B(y,y)}{\partial x} \cdot \frac{\partial D(y,t)}{\partial y} \, dy
\]

(1)

where \(D(x,t)\) is the mass fraction of particles less than size \(x\), \(t\) is the time of batch grinding, \(x\) is the size of particle to be broken and \(x_{\text{max}}\) is the maximum particle size present. \(S(x)\) is the specific rate of breakage (fracture) representing the probability of particle of size \(x\) to be selected for breakage and \(B(x,y)\) is the cumulative primary (fracture) breakage distribution equal to mass fraction of fragment sizes less than \(x\) produced from particles of size \(y\). Assuming that the product of selection and breakage function is of the following form:

\[
S(x) \cdot B(y,x) = K x^n \cdot \left(\frac{y}{x}\right)^m
\]

(2)

Nakajima and Tanaka [9] obtained analytical solution of the batch grinding equation (Eq. 1) in cumulative oversize form:

\[
R(x,t) \approx R(x,0) \cdot \exp\left[-(\mu K x^n t)^\nu\right] \quad \text{for} \ m \neq n
\]

(3)

\[
R(x,t) = R(x,0) \cdot \exp(-K x^n t) \quad \text{for} \ m = n
\]

(4)

where \(m\) and \(n\) are constants, \(K\) is the grinding rate constant, and \(\mu\) and \(\nu\) are determined by the \(m/n\) ratio.

**Results and discussion**

![Fig. 1. DTA curves of premullite powder samples grinded for various times. Curves are shifted for visualization purpose.](image1)

![Fig. 2. Powder XRD patterns of the feed sample heat treated to a various temperatures.](image2)

The crystallization path of calcined premullite powders was examined by DTA. The DTA curve of as-received sample prior to calcinations (Fig. 1) is characterized with the peaks in the low temperature range, caused by dehydration, dehydroxylation and decomposition of nitrates and alkoxides and the combustion of organics [10], which correspond to a great mass loss in this temperature area. The DSC curve is further characterized with exotherms at 978°C and 1250°C. The diphasic gel contains polycondensed and polymerized particles without sufficient homogeneity for direct mullite formation below 1000°C. Instead, primary crystallization Al-Si spinel occurs followed by mullite crystallization at ~1200°C. In DTA scans of samples calcinated at 700°C for 2 h, milled for various time and re-calcinated the low-temperature region, endothermal peaks, except the peak due to a dehydration, are missing and high-temperature exothermal peaks are more pronounced due to an increased concentration.
In order to assign the DSC exothermic events and to establish the crystallization path of the gel, the samples were thermally treated for 4 hours at various temperatures and then subjected to XRD analysis. XRD patterns of non-milled sample specimens are shown in Fig. 2, as an example. Analysis reveal that the gel is amorphous up to the first exotherm on DSC curve at 977°C, after this point the XRD pattern displays typically broad reflections attributable to weakly crystallized aluminosilicate spinel. As evidenced by XRD, spinel phase transforms into orthorhombic mullite at temperatures below 1300 °C. The gel thermal evolution corresponds to type III precursors according to Schneider’s classification formation path [4]. At 1300°C and 1600°C an α-alumina lines could be seen. That is the consequence of initial stoichiometry positioned in mullite+alumina phase field of Al₂O₃-SiO₂ phase diagram.

Fig. 3 shows product particle size distributions for the pre-mullite calcined gel obtained at various grinding times in the planetary ball mill. As can be seen, size distribution shifts progressively to finer sizes with the increase of grinding interval. The shift is slightly better pronounced at low comminution duration. The shape of the size distribution curve of feed sample indicates bimodal size distribution. The size distribution of samples grinded for 15 and 30 min is also bimodal but less expressed than for feed sample. With further increase
of grinding time the curves become monomodal reflecting samples monodisperse distribution.

For a detailed view of the size and morphology of the particles, SEM investigation of the powders was carried out. Fig. 4 shows the SEM micrographs of the feed sample (Fig. 4a) and powder milled for 512 min (Fig. 4c). Feed sample, as well as grinded sample, is characterized with particles of irregular shape. As far as it can be estimated, the particle size obtained by the Coulter Counter correlates with calcined powders particle sizes.

Analysis of grinding data was performed according to Eq. (3), previously converted to linear form by taking the logarithm of both sides [5-8]:

$$
\ln \left[ -\ln \left( \frac{R(x,t)}{R(x,0)} \right) \right] = \nu \ln(\mu K t) + n \nu \ln(x)
$$

(5)

where

$$
\nu \ln(\mu K t) = \nu \ln(\mu K) + \nu \ln(t)
$$

(6)

As can be seen in Fig. 5a linear dependence of normalized cumulative oversize functions, \( \ln\{-\ln[R(x,t)/R(x,0)]\} \), on particle size in logarithmic scale, \( \ln x \), exist only for data corresponding to grinding interval of 16, 32, 64 and 128 min. For increased duration of grinding, the data could not be fitted to Eq. 5. Therefore, the experimental data for extended grinding periods were not used in kinetic modeling.

Regression analysis of data corresponding to grinding interval of 16, 32, 64 and 128 min, using least-square method (Fig. 5a), resulted with constant value of \( n \nu \) (fixed to 3.18) and intercept \( \nu \ln(\mu K t) \) varying with time. The intersects of straight lines in Fig. 5a on the ordinate for grinding intervals of 16, 32, 64 and 128 min are plotted against the grinding time in Fig. 5b. Parameter \( \nu \) was then obtained as a slope from linear regression analysis of Eq. (6). Furthermore, model parameter \( \mu \) was obtained from Nakajima and Tanaka chart [9] using known values of \( \nu \) and \( m/n \) ratio. Finally, grinding rate constant was calculated from intercept value of Eq. (6) and known values of parameters \( \mu \) and \( \nu \). Grinding kinetics analysis of experimental data resulted with model suitable for prediction of particle size distribution during grinding of calcined pre-mullite gel in planetary ball mill:

$$
R(x,t) = R(x,0) \cdot \exp\left( -2 \cdot 10^{-6} x^{1.18} t^{1.076} \right)
$$

(7)

where \( x \) is the particle size in \( \mu m \), and \( t \) is the grinding time in minutes.
Conclusions

The kinetics of comminution of calcined pre-mullite gel in planetary ball mill was investigated. The grinding kinetics approach was successfully applied to the analysis of product size distribution.

A classical batch grinding equation was used for the modeling of comminution process. The analytical solution equation, as well as parameters of grinding kinetics was obtained through Nakajima and Tanaka approach.

Grinding kinetics analysis of experimental data resulted with model suitable for prediction of particle size distribution for grinding of calcined amorphous gel in planetary ball mill if the duration of grinding is no longer than 128 min.

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