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Structural-Phase Transformation Kinetics During Sintering of Alumina Ceramics using Metastable Nanopowders

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Abstract:
The processes taking place during pressureless sintering of nano-metastable $\text{Al}_2\text{O}_3$, compacted up to high densities (0.7 of the theoretical density) using the magnetic pulsed method were studied. The influence of MgO, TiO$_2$ and ZrO$_2$ additives on the kinetics of $\text{Al}_2\text{O}_3$ polymorphous transition, shrinkage and microstructure evolution during annealing at temperatures up to 1450°C has been studied. We have found that the process of annealing is two-staged starting with a polymorphous transition. Doping changes the starting temperature as well as the shrinkage depth at both stages. TiO$_2$ and ZrO$_2$ additives decrease the temperature of the onset of shrinkage, whereas MgO increases it. The best composition contained MgO in the series of examined types of ceramics with an $\alpha$-$\text{Al}_2\text{O}_3$ matrix. The positive role of Mg addition in the production of dense and hard $\text{Al}_2\text{O}_3$ ceramics is related to the nature of Mg influence on the activation of diffusion processes in $\text{Al}_2\text{O}_3$, as well as to the way of uniform distribution of MgO dopant in the material. All these factors provide effective damping of diffusion processes and limit $\alpha$-$\text{Al}_2\text{O}_3$ crystal growth. Highly dense MgO, ZrO$_2$ and TiO$_2$ doped $\text{Al}_2\text{O}_3$ ceramics with a grain size of 190, 220, and 250 nm and microhardness of 22, 17 and 17 GPa, correspondingly have been obtained.

Keywords: Alumina, sintering, magnetic pulse method, MgO, TiO$_2$ and ZrO$_2$ additives

Introduction

Due to accessibility and the unique combination of thermomechanical properties corundum seems to be a perspective material for a wide range of construction applications. The transition to a nanoscale structure promises essential improvement of the properties of corundum ceramics and expansion of the application sphere. Though sintering of corundum ceramics is complicated with polymorphous transitions and a high speed of recrystallization this leads to a large grain size and thus to high non-uniformity of the material and low mechanical properties [1,2].

A technique, which includes the use of nanosized powders and their compaction up to high densities, enabling a temperature decrease and shortening of the duration of ceramics sintering, possesses obvious advantages. Though poor compressibility of nanosized powders requires the use of high-energy methods of consolidation [3]. The magnetic-pulsed...
compaction (MPC) method, used in the present work, provides high (~0.7) relative density of nanopowder compacts and also mechanically activates the material and increases the stable modification content [4]. Besides, the technique of limiting corundum crystal growth by insertion of small additives into the material, which form the second phase during sintering, is well known [5]. Due to its different solubility in starting metastable modifications of $\text{Al}_2\text{O}_3$ and in the formed corundum, $\text{MgO}$ [6] is of especial interest. Also, the influence of additives of titania and zirconia appears to be interesting [5,7].

In the present study the research of alumina structural-phase transitions in the controlled processes of thermal annealing of nanopowder samples of pure alumina as well as alumina with additions of magnesia (2.6 mass%), titania (1 mass %) and zirconia (10 mass%), compacted up to high green density was made. High density of green bodies, achieved by MPC, as well as doping, allowed sintering of ceramics with a fine-grained structure.

**Experimental methods**

The research included the MPC of nanopowders, annealing of the ceramic samples, investigation of the structure and the phase content of the ceramics, measuring of microhardness. The characteristics of nanopowders, used in the investigation for ceramics sintering are presented in table. I (Pulsed processes laboratory, Institute of Electrophysics, UD RAS). The powders were produced by the method of electrical explosion of wire (EEW) followed by sedimentation in isopropanol, providing removal of large particle fractions with sizes greater than 200 nm [9]. AT1 and AZ10 powders are the mechanical mixtures, prepared by cosedimentation of $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ or $\text{ZrO}_2$ nanopowders correspondingly. The AM1-1 powder was produced by EEW of the alloy (Al+1.3 mass% Mg) with the following sedimentation. Phases containing Mg were not detected in its composition. Hypothetically, Mg atoms take places of Al in the $\gamma$-$\text{Al}_2\text{O}_3$ crystalline lattice. Due to the production method, the distribution of the alloy additive in the AM1-1 powder is more uniform compared to AT1 and AZ10 powders. Considerable contents of metastable phases are characteristic for all used nanopowder oxides: specifically, $\text{Al}_2\text{O}_3$ consisted of metastable $\gamma$- and $\delta$- modifications, $\text{TiO}_2$ contained a large amount of anatase and $\text{ZrO}_2$ – a tetragonal modification. All the powders are characterized mainly by spherical shaped particles, a wide spectrum of size distributions and weak agglomeration [8,9].

The powders were compacted by the MPC method with pressure pulses with amplitudes up to 1.2 GPa. The compacts were disk-shaped with the diameter of 30 mm and 3.5 mm thick and relative density of ~0.7 [10]. The X-ray diffraction investigation indicates intensive mechanical activation of the material in terms of additional band broadening of X-ray diffraction lines as well as the increase of the more stable modifications content.

Annealing of the ceramic items was realized in air at temperatures of up to 1450°C in an electroresistive furnace with controlled heating and cooling.

The phase content, microdistortions and crystallite size, $d_\chi$, were investigated by the X-ray diffraction method (DRON-4). The crystalline size $d_\chi$ was determined by X-ray diffraction band broadening using the Sherer-Selyakov technique. The ceramics fracture microstructure was investigated by atomic-force microscopy (AFM) (Solver 47). The microhardness of the ceramics in the terms of Vickers, $H_v$, the specific surface area, $S_{\text{BET}}$, were determined using standard methods. The sample’s density was measured by hydrostatic weighting.
Table I Characteristics of the precursor powders.

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Mixing proportion, mass.%</th>
<th>Phase content, mass.%</th>
<th>d_x nm</th>
<th>S_BET m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1-1</td>
<td>-</td>
<td>Al₂O₃: 33 γ + 67 δ TiO₂: 66 A + 34 R</td>
<td>18 - δ</td>
<td>69</td>
</tr>
<tr>
<td>AT1</td>
<td>99 (Al₂O₃) + 1 (TiO₂)</td>
<td>Al₂O₃: 45 γ + 55 δ ZrO₂: 61 M + 39 T</td>
<td>22 - δ</td>
<td>56</td>
</tr>
<tr>
<td>AZ10</td>
<td>90 (Al₂O₃) + 10 (ZrO₂)</td>
<td>Al₂O₃: 33 γ + 67 δ TiO₂: 66 A + 34 R</td>
<td>22 - δ</td>
<td>72</td>
</tr>
</tbody>
</table>

Note: γ and δ - polymorphs of Al₂O₃, A and R – polymorphs of TiO₂ anatase and rutile, M and T – monoclinic and tetragonal modifications of ZrO₂, d_x – crystallite size, evaluated using the X-ray data, S_BET – specific surface area using BET.

Table II Characteristics of annealing conditions, structure and properties of the ceramics samples.

<table>
<thead>
<tr>
<th>Ceramic type</th>
<th>Dopant</th>
<th>Phase content, mass.%</th>
<th>τ_s, min 1450°C</th>
<th>d nm</th>
<th>ρ</th>
<th>H_v GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1-1</td>
<td>MgO</td>
<td>96 - α-Al₂O₃, 4 - MgAl₂O₄</td>
<td>6</td>
<td>190</td>
<td>0.969</td>
<td>22</td>
</tr>
<tr>
<td>AT1</td>
<td>TiO₂</td>
<td>99 - α-Al₂O₃, 1 - R-TiO₂</td>
<td>6</td>
<td>350</td>
<td>0.961</td>
<td>17</td>
</tr>
<tr>
<td>AZ10</td>
<td>ZrO₂</td>
<td>90 - α-Al₂O₃, 7,5 - T-ZrO₂, 2,5 - M-ZrO₂</td>
<td>6</td>
<td>150</td>
<td>0.920</td>
<td>13</td>
</tr>
</tbody>
</table>

Note: : ρ - relative density, τ_s – annealing time, d – average size of polycrystalline blocks, evaluated using AFM data, γ and δ - polymorphs of Al₂O₃, A and R – polymorphs of TiO₂ anatase and rutile, M and T – monoclinic and tetragonal modifications of ZrO₂.

Results and discussion

A polymorphic transformation (γ+δ)→α, accompanied by volume change occurs during sintering of the precursor powder. Therefore shrinkage occurs in two stages (fig.1), and the first stage in temperature range T_A<T<T_B, corresponds to the polymorphic transformation, as detected by X-ray analysis [11].

The relative change of density during the polymorphic transformation is determined from the difference between theoetric densities of γ- and α-polymorphs:

\[
(\Delta \rho_R)_{PT} = (\rho_\alpha - \rho_\gamma) / \rho_\gamma = (3.987 - 3.66) / 3.66 = 0.0893
\]

or, in the case of linear isotropy shrinkage

\[
(\Delta L_R)_{PT} = 1 - 1 / \sqrt[3]{1 + (\Delta \rho_R)_{PT} + 1]} = 0.028.
\]

The shrinkage value (\(\Delta L_R\)) = 1 - (L_T/B/L_T_A) of all powders investigated exceeds the calculated value (\(\Delta L_R\))_{PT} (fig.2 b). Several investigators [6,12,13] noted a similar phenomenon of “hyper shrinkage” for polymorphous systems (Al₂O₃, TiO₂). The origin of such behavior is explained well by a model described in [6], where the change of crystalline volume during a polymorphous transformation leads to the appearance of nonsymmetrical forces, which move particles. The result of such movements is particle rearrangement resulting in closer packing. Thus, the observed shrinkage (\(\Delta L_R\)) in the temperature range T_A<T<T_B is the result of two
processes: polymorphous transformation and particle rearrangement and its value exceeds the calculated one - (\(\Delta L_R\))\(_{PT}\). It is worth mentioning, that the starting temperatures of shrinkage \(T_A\) correlated with (\(\Delta L_R\)) values (fig. 2a): addition of MgO increases \(T_A\), compared with pure \(Al_2O_3\), and the value of (\(\Delta L_R\)) is the highest (fig. 2b, AM1-1). On the other hand, additions of \(TiO_2\) and \(ZrO_2\) decrease \(T_A\) and the value (\(\Delta L_R\)) of considered powders is small (fig. 2b, AT1 and AZ10).

Fig. 1 Typical shrinkage curve of nano- \(Al_2O_3\) at constant heat rating. The range of polymorphic transformation is bordered with a dotted line.

Fig. 2 Features of shrinkage in the first stage of nano- \(Al_2O_3\), doped with MgO, \(TiO_2\), \(ZrO_2\): (a) – initial temperature of shrinkage (\(T_A\)); (b) – relative shrinkage (\(\Delta L_R\)) value in the first stage (\(T_A < T < T_B\))

Data, presented in fig. 3, show, that the evolution of crystalline size is governed by doping. Anomalous changes of corundum crystalline sizes were found in the \(TiO_2\) doped
Primary $\alpha$-crystals have dimensions that significantly exceed the size of crystals of the initial phases. However, in the temperature range of bulk $\alpha$-formation, a large number of crystals appeared to be comparable in the size with the crystals of the initial phases (fig. 3b). In the case of MgO doping first $\alpha$-crystals have sizes close to the size of crystals of the initial alumina phases (fig. 3a).

**Fig.3** Crystal size change of $\delta$- and $\alpha$-alumina during sintering of dense green bodies of nano- $\text{Al}_2\text{O}_3$, doped with MgO – (a), TiO$_2$ - (b)

Structural evolution during the final stage of sintering has been analyzed using AFM images of cleavage surfaces of ceramic items made in “height” (relief) and “Mac*Cos” (phase contrast) modes (figs. 4 and 5). In all cases the ceramic material consisted from polycrystalline blocks, and their shape and dimensions depended on doping. AFM data of the averaged block size, $d$, (see table II), demonstrates the restrictive effect of MgO and ZrO$_2$ additives on recrystallization of the $\text{Al}_2\text{O}_3$ matrix. Uniformly distributed, well contoured, light, 10-20 nm sized areas are well distinguished in AFM “Mac*Cos” images (fig. 4a). Probably the above-mentioned areas correspond to the second phase of $\text{MgAl}_2\text{O}_4$, previously determined by X-ray analysis. It is confirmed by an integrated analysis of the structure in “height” and “Mac*Cos” modes (fig. 5). Sharp peaks on the “Mac*Cos” profile curve (fig. 5c) and outlines of the relief corresponding to them testify of block non-homogeneity and hence, the non-single phase nature of blocks. The above-mentioned peculiarity remains valid with increased sintering duration (fig. 4b). Thus, the applied doping method enables sintering of fine-grained $\text{Al}_2\text{O}_3$ ceramics with a homogeneous structure and uniformly distributed nano-phase $\text{MgAl}_2\text{O}_4$.

The limiting effect of the ZrO$_2$ additive on recrystallization in $\text{Al}_2\text{O}_3$ is entirely different. Despite of the closeness of microstructure scales of AM1-1 and AZ10 (tab. II), the
structure of AZ10 is extremely non-uniform. AFM images display blocks of essentially different dimensions and a non-homogeneous admixture distribution (light areas in fig. 4c). The observable areas of the second phase are polycrystalline due to a large discrepancy between crystalline size values measured by X-ray and defined from AFM images. It is important to note, that ZrO$_2$ in the alumina matrix mainly exists in a tetragonal modification (75 %) with a mean crystalline size of 70 nm. A minor part of ZrO$_2$ is found in the monoclinic state with a mean crystalline size of 30 nm.

![AFM images of cleavage surfaces of ceramic items: AM1-1 ($\tau_s = 6$ min) (a), AM1-1 ($\tau_s = 30$ min) (b), AZ10 ($\tau_s = 60$ min) (c), AT1 ($\tau_s = 6$ min) (d) (“Mac*Cos” (phase contrast) mode).](image)

TiO$_2$ doped alumina ceramics is characterized with the largest block size (fig. 4 d). Their surface, compared to the ceramic types analyzed above, is smooth, implying the proximity of block and crystal dimensions. Clusters of the admixture phase are non-homogenously dispersed and located as layers 100 nm thick between alumina blocks (light areas in fig. 4d). Some isolated grains of similar dimensions also exist.

The distinctive feature of AM1-1 and AT1 ceramics is that the ceramic structure forms very fast. Prolongation of sintering has a weak effect on it. On the contrary, a long
duration of sintering is necessary for the formation of a dense structure in the case of ZrO$_2$ doping.

![AFM images of cleavage surfaces of ceramic items AM1-1 ($\tau_s = 6$ min): a - “height” mode; b - “Mac*Cos” mode, with corresponding crosssections profiles ($Y=800$ nm) - c.](image)

**Fig. 5** AFM images of cleavage surfaces of ceramic items AM1-1 ($\tau_s = 6$ min): a - “height” mode; b - “Mac*Cos” mode, with corresponding crosssections profiles ($Y=800$ nm) - c.

The microhardness of all ceramic groups investigated was in the range 17 – 22 GPa. The most hard ceramics was obtained in the case of MgO doping in a “short” regime.

All facts mentioned above testify the preference of MgO doped alumina ceramics among the $\alpha$-alumina matrix ceramics investigated. In our opinion, the beneficial role of magnesium in the formation of dense and hard alumina ceramics is related to both the nature of the dopant influence on the activation of diffusion, and the way of dopant introduction. Magnesium in the initial powder is solved in the alumina crystalline lattice and does not form an individual phase. It is only during sintering that the magnesium-containing admixture ($\text{MgAl}_2\text{O}_4$) is isolated at the surface of $\alpha$-alumina crystals. Uniformity of admixture distributing provides effective retarding of diffusion and limits $\alpha$-$\text{Al}_2\text{O}_3$ grain growth.

**Conclusions**

1. High green density (~0.7) enables sintering of high-dense sub-micron ceramics using metastable alumina nanopowders at relatively low temperatures -1450°C and the
duration of sintering of a few minutes. Near-fully dense alumina-based ceramics were sintered with MgO, ZrO$_2$ or TiO$_2$ additions with grain size of about 190, 220, 350 nm and microhardness of 22, 17, 17 GPa, respectively.

2. MgO is the most effective additive restricting $\alpha$-Al$_2$O$_3$ grain growth among the dopants: MgO, ZrO$_2$, TiO$_2$. Zirconia doping limits $\alpha$-Al$_2$O$_3$ grain growth too, but a long sintering duration at elevated temperatures is necessary for producing high-dense ceramics.

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References


Резюме: Изучены процессы, протекающие в ходе спекания нанометастабильного $\text{Al}_2\text{O}_3$ без давления предварительно уплотненного до высокой плотности (0,7 теоретической плотности) с применением метода пульсаций магнитного поля. Исследовано влияние добавок $\text{MgO}$, $\text{TiO}_2$ и $\text{ZrO}_2$ на кинетику полиморфного перехода, усадку и развитие микроструктуры $\text{Al}_2\text{O}_3$ в процессе отжига до 1450°C. Установлено, что процесс отжига двухстадийный, начиная с полиморфного перехода. Введение добавок изменяет исходную температуру и усадку обеих фаз. Добавки $\text{TiO}_2$ и $\text{ZrO}_2$ понижают температуру усадки, в то время как $\text{MgO}$ температурой повышает. Самый лучший состав среди исследованных типов керамики с матрицей $\alpha$-$\text{Al}_2\text{O}_3$ содержал $\text{MgO}$. Положительная роль добавления $\text{MgO}$ при получении плотной и твердой $\text{Al}_2\text{O}_3$ керамики касается влияния $\text{MgO}$ на активацию процесса диффузии в $\text{Al}_2\text{O}_3$, а также способа однородности распределения добавки $\text{MgO}$ в материале. Все изложенные факторы позволяют эффективное торможение процесса диффузии и ограничивают рост кристаллов $\alpha$-$\text{Al}_2\text{O}_3$. Получена керамика $\text{Al}_2\text{O}_3$ высокой плотности с добавками $\text{MgO}$, $\text{ZrO}_2$ и $\text{TiO}_2$, размер зерен к которому составлял 190, 220 и 250 нм, микротвердость 22,17 и 17 ГПа.

Ключевые слова: Глинозем, спекание, метод пульсаций магнитного поля, добавки $\text{MgO}$, $\text{TiO}_2$, $\text{ZrO}_2$.

Садржај: Проучени су процеси који се одвијају током синтеровања нанометастабилног $\text{Al}_2\text{O}_3$ без притиска, који је компактиран до велике густине (0,7 теоријске густине) применом метода пулсирања магнитног поља. Проучен је утицај адитива $\text{MgO}$, $\text{TiO}_2$ и $\text{ZrO}_2$ на кинетику полиморфног прелаза, скупљања и развоја микроструктуре $\text{Al}_2\text{O}_3$ током одмеравања до 1450°C. Утврђено је да се процес одмеравања одвија у два стадијума и започиње полиморфним прелазом. Дотирање лепа почетну温度тура, као и скупљање за обе фазе. Адитиви $\text{TiO}_2$ и $\text{ZrO}_2$ снажавају температурну почетну скупљања, док је $\text{MgO}$ повишава. Најбоља композиција у низу проучених типова керамике са $\alpha$-$\text{Al}_2\text{O}_3$ матрицом садржала је $\text{MgO}$. Позитивна улога добављања $\text{MgO}$ у производи густине и тврде $\text{Al}_2\text{O}_3$ керамике односи се на природу утицаја $\text{Mg}$ на активацију процеса диффузии у $\text{Al}_2\text{O}_3$, као и начин унформне дистрибуције допанта $\text{MgO}$ у материјалу. Сви изложене фактори омогућавају ефективно пругање процеса диффузии и ограничавају раст кристала $\alpha$-$\text{Al}_2\text{O}_3$. Добављена је $\text{Al}_2\text{O}_3$ керамика високе густине допирања са $\text{MgO}$, $\text{ZrO}_2$ и $\text{TiO}_2$ са великом зрен од 190, 220 и 250 нм и микротврдности од 22, 17 и 17 ГПа.

Ключне речи: Алумина, синтеровање, метода пулсирања магнитног поља, $\text{MgO}$, $\text{TiO}_2$ и $\text{ZrO}_2$ адитиви.