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Formation and Mechanical Properties of Alumina Ceramics Based on Al_2O_3 Micro- and Nanoparticles

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Abstract—Alumina micro- and nanopowders with the particle size from 200 μm to 40 nm synthesized by the sol-gel method are studied. The particle size dependence of γ-Al_2O_3→α-Al_2O_3 phase transformation is studied by differential thermal analysis, X-ray diffraction method, and transmission electron microscopy. X-ray diffraction data show that for alumina nanoparticles γ-Al_2O_3→θ-Al_2O_3 phase transformation occurs at 900°C, and for microparticles it occurs in the temperature range 1150–1200°C. The alumina ceramics produced of alumina nanoparticles is shown to have higher flexural strength under three-point bending than the ceramics produced of microparticles. The obtained results demonstrate that alumina particle size reduction stabilizes the formation of α-Al_2O_3 at lower temperatures, due to which the grain growth rate decreases and the flexural strength of monolithic oxide ceramics increases.

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1. INTRODUCTION

A central task in modern materials science is the development of new materials with improved functional properties. Ceramic composites on the basis of oxide matrices are attractive for applications where metallic materials have tendency to creep and oxidation. Aluminum oxide is one of the most promising ceramic materials for various applications under extreme operating conditions owing to its high hardness, thermal and chemical stability combined with availability and low cost. However, the use of alumina matrix materials under thermal loading conditions is limited due to low impact toughness typical of ceramics. Rapid cracking under impact loading reduces the reliability of the materials. This necessitates additional research on cracking mechanisms in materials with different reinforcing agents for oxide matrices and on treatment methods that increase the flexural strength and impact toughness of the materials [1–11].

The currently available Al_2O_3-based ceramics with coarse-grained structure are brittle, have low cracking stability, and high sensitivity to erosive and abrasive wear—the factors that greatly limit their application. The mechanical properties of ceramics, including Al_2O_3-based ones, can be enhanced significantly if the developed material has fine homogeneous structure, ultimate density, high hardness, and cracking stability [1, 2]. Today, the use of nanoparticles for the improvement of material characteristics is gaining momentum in the design of ceramics. By altering particle size and shape, the properties of the final product can be increased significantly.

At a given phase composition it is important to synthesize ceramics that has highly homogeneous nanostructure with the smallest possible grain size, minimum porosity, and well-defined grain boundaries [3, 4]. These conditions usually provide good mechanical properties (strength, hardness) of ceramics.

It is known that the strength of monolithic oxide ceramics can be increased if two main problems are solved: (i) achievement of maximum nanophase content to reduce creep, which makes the initial defect size comparable to the grain size, and (ii) introduction of a dispersed phase to neutralize present or generated defects [2]. The next step in improving the properties of nanostructured ceramics (increase of impact toughness) is the addition of a strengthening phase, i.e., development (design) of new composite ceramics [10–17].

The aim of this paper is to study the conditions of ceramics nanostructuring by the sol-gel method and to study phase transformations and mechanical properties of alumina produced of different-sized particles (from micro- to nanoparticles).

2. EXPERIMENTAL

In the paper, two sets of fine-grained alumina samples (with micro- and nanoparticles) were synthesized and investigated.

The first set of fine-grained alumina samples with micron-sized particles was prepared by the standard solution precipitation method, in which sodium aluminate was chosen as the precursor, and NaOH or ammonia solution was used as the precipitator [8].

The second set of samples was produced by a modified mesoporous silica synthesis technique with the use of surfactants [8, 9]. Our sol-gel synthesis of alumina nanoparticles included the following stages: sodium aluminate synthesis and subsequent hydrolysis with the pre-addition of nuclei particles and a stabilizing agent solution (PEG-20000) into the reaction vessel. The resultant solution was kept at 20°C for 24 h. The precipitate was filtered in vacuum, rinsed several times in distilled water and ethanol.

The sets of synthesized precipitate samples were dried in a drying oven at 80°C for 36 h. Then, AlOOH (boehmite) powders were heated up in air at required temperature. The thermal behavior of the samples was investigated by differential thermal analysis on a Setaram TGA92 analyzer at the heating rate 10°C/min. The specific surface area of fine-grained Al_2O_3 was determined by the BET method (low-temperature nitrogen adsorption). The volume fraction of particles of a particular size in a sample was determined by laser diffraction (laser scattering). The particle size of the two sets of samples was defined using a laser diffraction particle size analyzer Horiba Partica LA-950. Additionally, the particle size of the two synthesized alumina powder sets after temperature treatment was determined on a scanning electron microscope JSM-6700, JEOL (Japan).

At the next stage, the powders were compacted and sintered to produce a nonporous ceramic material. A binder (TiO_2 powder) was added to powder for better sintering. Then, an organic additive (wax) was introduced into the obtained α-Al_2O_3 mixture to aid compaction and then the components were mixed in a vibration mill. Prior to compaction, the obtained mixture was thermally treated at 1300°C. Preliminary compaction was performed at the pressure $P = 250$ MPa. This stage was necessary to produce a material with low porosity. Then, the material was thermally treated again at 1300°C and finally compacted at $P = 450$ MPa. The final stage was sintering at 1450°C for 3 h.

To control the structural properties of the compacted samples, apparent porosity Π_0 and mean density ρ_m were determined by hydrostatic weighing. The determination accuracy was 0.01 g/cm for mean density and 0.1% for apparent porosity.

The material structure was examined by scanning electron microscopy (LEO 982). X-ray diffraction analysis was carried out on a diffractometer DRON-4 using filtered CuK$_\alpha$ radiation. The ceramics strength was determined on samples of standard shape on a tensile testing machine AG-50KNXD (Japan).

3. RESULTS AND DISCUSSION

Using the data obtained in aluminum hydroxide precipitation at constant pH, we studied the influence of precipitation conditions on the chemical composition and specific surface area of aluminum hydroxide derived from $Al(NO_3)_3$ and ammonia (Table 1).

The following phase transformations were studied: AlOOH (boehmite)$\rightarrow\gamma$-$Al_2O_3\rightarrow\delta$-$Al_2O_3\rightarrow\theta$-$Al_2O_3\rightarrow$ α-Al_2O_3 in samples heated from temperature 500°C (γ-Al_2O_3 formation temperature) to 1300°C.

Table 1. Effect of precipitation conditions on specific surface area and phase composition of samples after heating at temperature 200°C

Microparticles				Nanoparticles			
precipitation conditions		characteristic		precipitation conditions		characteristic	
pH	t, °C	S, m^2/g	phase composition	pH	t, °C	S, m^2/g	phase composition
7	50	60	Amorphous	10	30	156	Amorphous
9	70	85	Amorphous	12	30	180	Amorphous
	50	110	Amorphous				
	70	130	Amorphous				

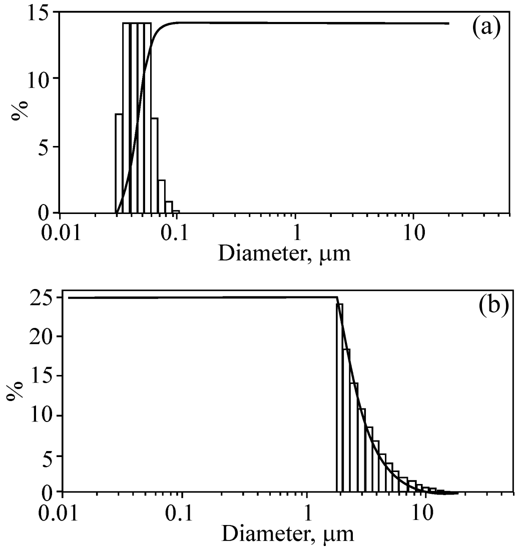

Fig. 1. Particle size distribution histogram of alumina after heating at temperature 500°C: samples with nano- (a) and microparticles (b).

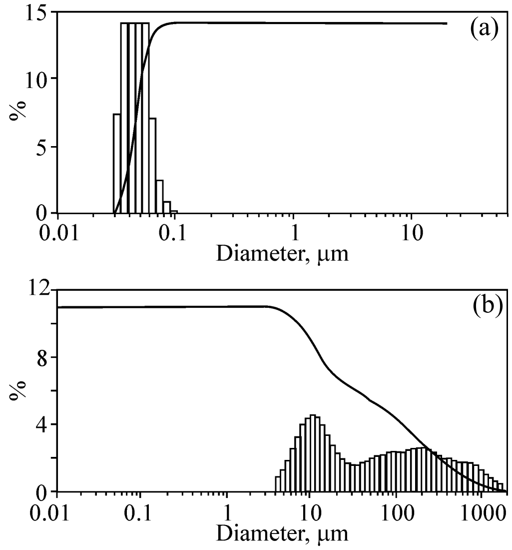

Fig. 2. Particle size distribution histogram of alumina after heating at temperature 900°C: samples with nano- (a) and microparticles (b).

As follows from the tabulated data, the samples with nanoparticles have larger specific surface area due to smaller particle size. Analysis of γ-Al_2O_3 particle size (heating temperature 500°C) on a laser particle analyzer confirmed the presence of 40–80 nm nanoparticles in the samples with nanoparticles (Fig. 1a) and 3–5 μm microparticles in the samples with microparticles (Fig. 1b).

In the both sets of samples, intensive aggregation processes take place with heating temperature growth above 900°C. The distribution curves show that the average aggregate size is ~0.5–0.8 μm for the samples with nanoparticles and ~10–100 μm for the samples with microparticles (Fig. 2).

Figure 3 illustrates the differential thermal analysis data that show different behavior of the samples with nano- and micro-sized particles at their thermal treatment up to 1250°C.

It follows from the figures that intensive polymorphous ($\gamma \rightarrow \delta \rightarrow \theta$)-$Al_2O_3$ transformations occur in the set with microparticles at a temperature of about 800°C, while in the set with nanoparticles these transformations occur earlier, with a more pronounced transition to α-alumina in the samples with nanoparticles. The performed microscopic examination of the alumina nano- and micropowders confirmed the difference in the size of oxide particles (Fig. 4).

According to scanning electron microscopy data on the particle size in the both sets of samples heated at 900°C, the average size of nanoparticles is ~150 nm (Fig. 4a) and that of microparticles is ~150–200 μm (Fig. 4b).

X-ray diffraction analysis of the samples with nano- and microparticles has revealed the following fundamental differences: the temperatures of transition between different crystalline modifications for the samples with nanoparticles are lower than for the samples with microparticles.

The main feature is the presence of well-defined peaks in the diffraction pattern of a nano-sized alumina

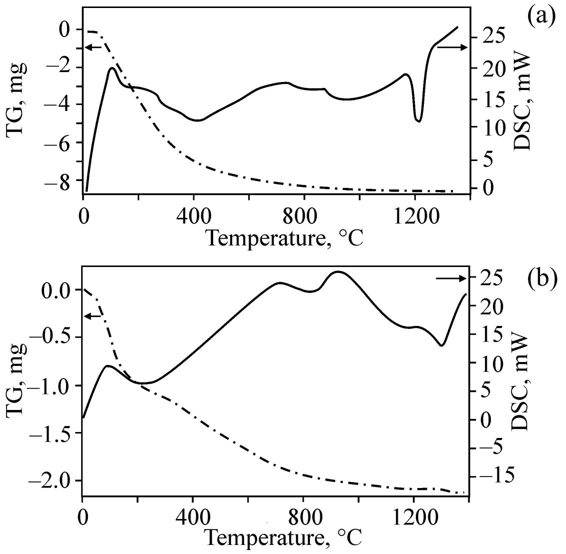

Fig. 3. Differential thermal analysis data for a sample with nano- (a) and microparticles (b) at thermal treatment up to 1250°C. DSC—differential scanning calorimetry, TG—thermogravimetry.

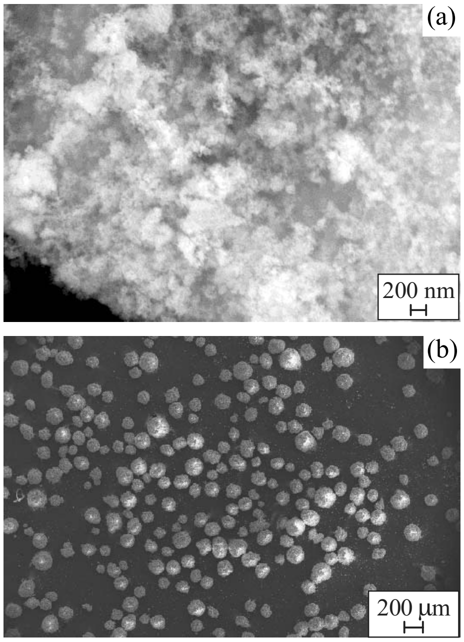

Fig. 4. Scanning electron microscopy data on the particle size of samples heated at temperature 900°C: ~150 nm for nanoparticles (a), ~150–200 μm for microparticles (b).

sample heated at 900°C—its diffraction pattern closely resembles the diffraction pattern of α-Al_2O_3 modification (Fig. 5a).

The diffraction pattern of the nano-sized alumina sample subjected to thermal treatment at 1150°C almost coincides with the diffraction pattern of α-Al_2O_3 modification and remains unchanged after heating at 1300°C. As for a micron-sized alumina sample, the diffraction patterns after heating at 500 and 900°C do not differ drastically (Fig. 5b). This is due to the fact that the transition of micron-sized alumina to the stable α-Al_2O_3 phase takes place at a temperature of 1200°C and higher.

Mechanical properties were estimated using two sets of samples: (i) alumina ceramics samples produced with alumina nanopowder, and (ii) alumina ceramics samples prepared with micron-sized alumina particles. The obtained results are given in Table 2.

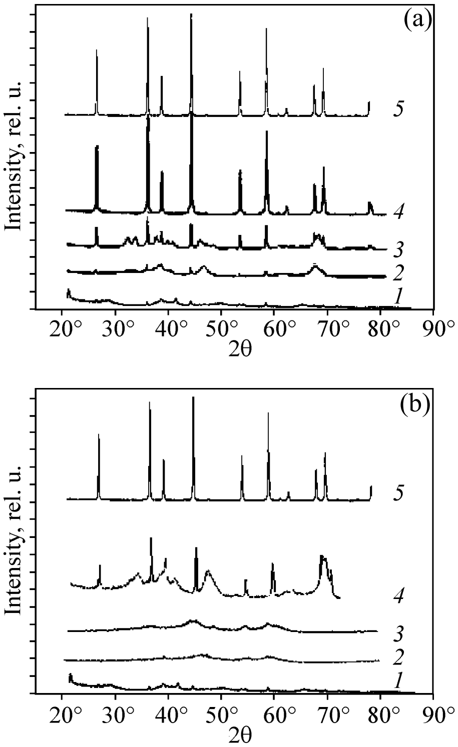

Fig. 5. X-ray diffraction patterns of samples with nano- (a) and microparticles (b) heated at different temperature: dry gel (*1*), 500 (*2*), 900 (*3*), 1150 (*4*), 1300°C (*5*).

The data in Table 2 demonstrate that the use of alumina nanoparticles as precursors/initial reagents for consolidated material increases the ultimate strength in three-point bending.

In general, the results show that particle size reduction stabilizes the formation of α-Al_2O_3 at lower temperatures, which impedes grain growth and noticeably increases the strength of monolithic alumina ceramics.

4. CONCLUSION

The influence of the particle size of alumina micro- and nanopowders with the particle size from 200 μm to 40 nm on γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ phase transformation has

Table 2. Comparison data on mechanical properties of alumina ceramics

Sample	Compaction conditions		Residual internal porosity, %	Density ρ, g/cm³	Flexural strength, MPa
	T, °C	*P*, MPa			
α-Al_2O_3, micro	1300	450	8	3.96	280
α-Al_2O_3, micro	1450	450	8	3.96	310
α-Al_2O_3, nano	1300	450	6	3.91	395
α-Al_2O_3, nano	1450	450	5	4.04	420

been studied by differential thermal analysis, X-ray diffraction, and transmission electron microscopy.

It is found that the use of alumina nanoparticles as the initial substance in the synthesis of alumina ceramics reduces the crystallite size of the ceramic material.

The particle size reduction in alumina nanopowders stabilizes α-Al_2O_3 formation at lower temperatures, due to which the grain growth rate decreases and the strength of monolithic alumina ceramics increases.

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