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Influence of sintering technology on structure and properties of alumina composite ceramics containing barium hexaaluminate

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Composite ceramics based on alumina with 15 mass% barium hexaaluminate obtained by hot pressing, pressureless and spark plasma sintering have been studied. The highest relative density (97.5 ± 0.2 % of theoretical) was obtained for the composite sintered by hot pressing. The smallest average size of Al_2O_3-grains ($0.9 \pm 0.1\,\mu$m) is observed for the material obtained by pressureless sintering. The highest fracture toughness (5.7 MPa $\cdot$ m$^{1/2}$ and 5.74 MPa$\cdot$m$^{1/2}$) possesses the materials obtained by pressureless sintering and hot pressing.

Keywords: hot pressing, spark plasma sintering, pressureless sintering, barium hexaaluminate, fracture toughness.

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Alumina-based composite ceramics with hexaaluminates of various chemical compositions are of interest due to the combination of high hardness, wear resistance, and chemical and thermal stability [1]. The tool industry (e.g., the production of replaceable cutting plates) is the potential field of application for such materials. Alumina provides high hardness and wear resistance, and hexaaluminates increase significantly the fracture toughness of materials [2]. The influence of barium hexaaluminate on the properties of oxide ceramics is of particular research interest at present. It is believed that this compound is more thermally stable than hexaaluminates of other chemical compositions [3]. In addition, this compound is the least studied.

It should be noted that hexaaluminates form *in situ* in the process of sintering, since their crystals have a prismatic shape and their introduction into the initial powder mixture is impractical due to the high probability of destruction of platelets during grinding or pressing. This is the reason why oxides, carbonates, or nitrates, which start to interact with alumina when heated to high temperatures, are used as the initial hexaaluminate-forming additives [4]. The sintering conditions may have a significant impact on the features of structure formation of prismatic grains of hexaaluminates. Therefore, the study of specifics of the formation of barium hexaaluminate in the process of sintering without pressure, with the application of external pressure, and with the passage of current through the sample is of particular interest. Thus, the aim of the present study is to examine the influence of pressureless sintering, hot pressing, and spark plasma sintering techniques on the features of structure formation of barium hexaaluminate in an alumina matrix and, accordingly, on the change in density, porosity, hardness, and fracture toughness of the obtained composites.

Alumina (99 % pure with an average particle size of 140 ± 50 nm) and barium oxide (99 % pure with an average particle size of $2.7 \pm 0.6\,\mu$m) powders were used to obtain experimental composite materials. Suspensions with a liquid content of 50 % were prepared for dispersing the initial powders. The barium oxide content was set to 3 mass% with a view to obtain 15 mass% of barium hexaaluminate in sintered materials. The design barium hexaaluminate content was chosen based on literature data, which suggest that a higher proportion of hexaaluminates may have a negative influence on fracture toughness due to the high porosity of materials [5]. The synthesis of composites with a lower barium hexaaluminate content is impractical in the present case, since it may become hard to assess the actual effect of the additive on the properties of the materials being studied. A ball mill was used for dispersing, which took 10 h. Grinding bodies made of alumina with a diameter of 3 mm were used. Following dispersion, a binder (polyvinyl alcohol) and a plasticizer (polyethylene glycol) were introduced into the suspensions prepared for material synthesis by pressureless sintering. A granulated powder was prepared by drying the suspension on a stove with subsequent grinding and sifting of the resulting granules. The granulated powder with particles $100-250\,\mu$m in size was then formed by uniaxial pressing under a pressure of 100 MPa. The suspensions prepared for hot pressing and spark plasma sintering were dried at a temperature below 100 °C.

Pressureless sintering of pressed samples in the form of beams was performed in a tubular furnace at a temperature of 1520 °C for 2 h. Hot uniaxial pressing was carried out at a temperature of 1520 °C under a pressure of 20 MPa for 20 min using a setup constructed by the Technological Design Institute of Scientific Instrument Engineering of the

Siberian Branch of the Russian Academy of Sciences at the Institute of Theoretical and Applied Mechanics of the Novosibirsk State Technical University. An MS-1 setup was used to perform spark plasma sintering at a temperature of 1500 °C under a pressure of 17 MPa for 5 min.

The apparent density and open porosity of the sintered materials were determined by hydrostatic weighing in accordance with GOST 2409–2014. The apparent density was calculated as the ratio of the dry sample mass and the mass difference between a water-saturated sample and a sample immersed in liquid. X-ray diffraction analysis was performed using an ADANI PowDix 600 diffractometer in $CuK_{\alpha_{1+2}}$-radiation. The ICDD PDF 4+ database was used for phase identification. Thin sections for structural studies, which were performed using a Carl Zeiss EVO 50 scanning electron microscope fitted with an electron probe microanalysis attachment, were prepared in accordance with the conventional procedure. Thermal etching was performed at a temperature 200 °C lower than the sintering one. To improve conductivity, a thin layer of gold was deposited onto the samples using a DSCR coater prior to their examination.

The Vickers hardness and indentation fracture toughness were measured with an SV-50A hardness tester under a load of 2 kg (for materials obtained by spark plasma sintering) or 5 kg (for materials synthesized by pressureless sintering and hot pressing). The load was chosen empirically so as to ensure the formation of sufficiently long cracks for fracture toughness measurements. The following formula was used to calculate the critical stress intensity factor [6]:

$$K_{Ic} = 0.048\left(\frac{c}{a}\right)^{-0.5}\left(\frac{H_v}{E\Phi}\right)^{-0.4}\frac{H_v a^{0.5}}{\Phi}\left[\mathrm{MPa}\cdot\mathrm{m}^{1/2}\right],$$

where H_v is hardness [GPa], E is the Young's modulus [GPa], a is the indentation semi-diagonal [μm], c is the length of a radial crack measured from the center of the indentation [μm], and Φ is a constant ($\Phi = 3$).

The results of X-ray diffraction analysis revealed the presence of α-Al_2O_3 and $Ba_{0.83}Al_{11}O_{17.33}$ phases in all materials (Fig. 1). Thus, it was demonstrated that the processes of barium hexaaluminate phase formation were completed in all materials. The sintering techniques had no effect on the phase composition.

The properties of the examined materials are listed in the table. The highest values of density (relative to the theoretical one) were found in composite ceramics obtained by hot pressing. The composite synthesized by pressureless sintering is characterized by the lowest apparent density. This dependence illustrates the efficiency of pressure sintering in fabrication of high-density ceramics. At the same time, the material prepared by spark plasma sintering had the highest value of open porosity.

Structural studies revealed the specifics of the grain structure of materials (Fig. 2). All materials contain equiaxed dark alumina grains and light grains of a prismatic shape. According to the electron probe microanalysis data, the latter grains consist of Ba, O, and Al; therefore, they correspond to barium hexaaluminate (Fig. 2, *d*). The average alumina grain size was the smallest ($0.9 \pm 0.1\,\mu$m) in the material obtained by pressureless sintering and the highest ($1.5 \pm 0.1\,\mu$m) in the composite prepared by spark plasma sintering. The noted features are indicative of intensification of sintering processes under the application of pressure and electric current to the sample.

It is evident that the specifics of formation of barium hexaaluminate platelets in the structure of composites depend on the sintering technique. Specifically, clusters of barium hexaaluminate up to 8 μm in length oriented transversely to the applied load formed in the materials prepared by hot pressing. The direction of load application is indicated by the arrow in Fig. 2, *a*.

The material obtained by spark plasma sintering (Fig. 2, *b*) did also contain barium hexaaluminate clusters, but featured a greater number of separate platelets. The orientation of barium hexaaluminate grains does not depend on the direction of load application. In the structure of the material synthesized by pressureless sintering, platy grains are distributed most uniformly, and large clusters are lacking. The magnified image of the structure in Fig. 2, *c* demonstrates that certain platelets consist of two layers (i. e., two platelets that were joined along their basal plane in the process of sintering [7]). Elsewhere, microcracks, which form due to the difference in linear thermal expansion coefficients of barium hexaaluminate platelets and Al_2O_3-matrix grains, are seen running along these platelets.

The material prepared by pressureless sintering has the highest number of pores in the structure. However, they are significantly smaller in size than those present in the composite obtained by spark plasma sintering. It is likely that the growth of intergranular pores is attributable to

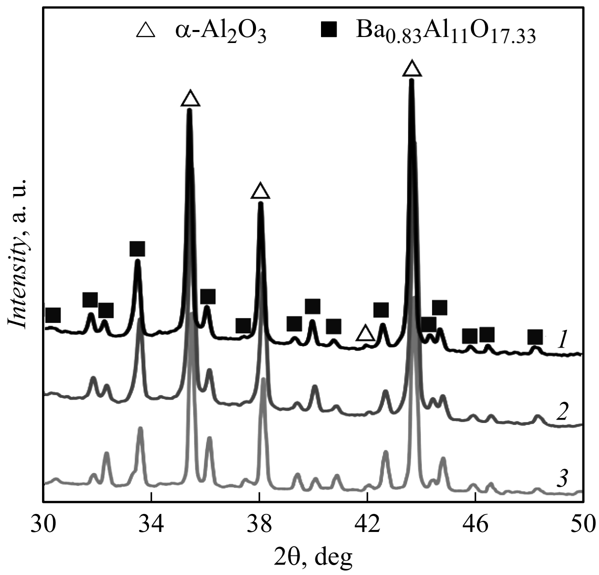

Figure 1. X-ray diffraction patterns of the studied materials synthesized using different methods: *1* — hot pressing, *2* — spark plasma sintering, and *3* — pressureless sintering.

Properties of the studied sintered materials

Sintering method	Apparent density, g/cm^3	Density relative to the theoretical one, %	Open porosity, %	Hardness, H_{v2}	Critical stress intensity factor, MPa $\cdot$ m$^{1/2}$
Hot pressing	3.91 ± 0.02	97.5 ± 0.2	0.4 ± 0.1	1740 ± 33	5.7 ± 0.1
Spark plasma sintering	3.86 ± 0.03	96.4 ± 0.4	2.1 ± 0.1	2085 ± 33	4.9 ± 0.1
Pressureless sintering	3.84 ± 0.03	95.8 ± 0.4	0.2 ± 0.1	1840 ± 16	5.7 ± 0.1

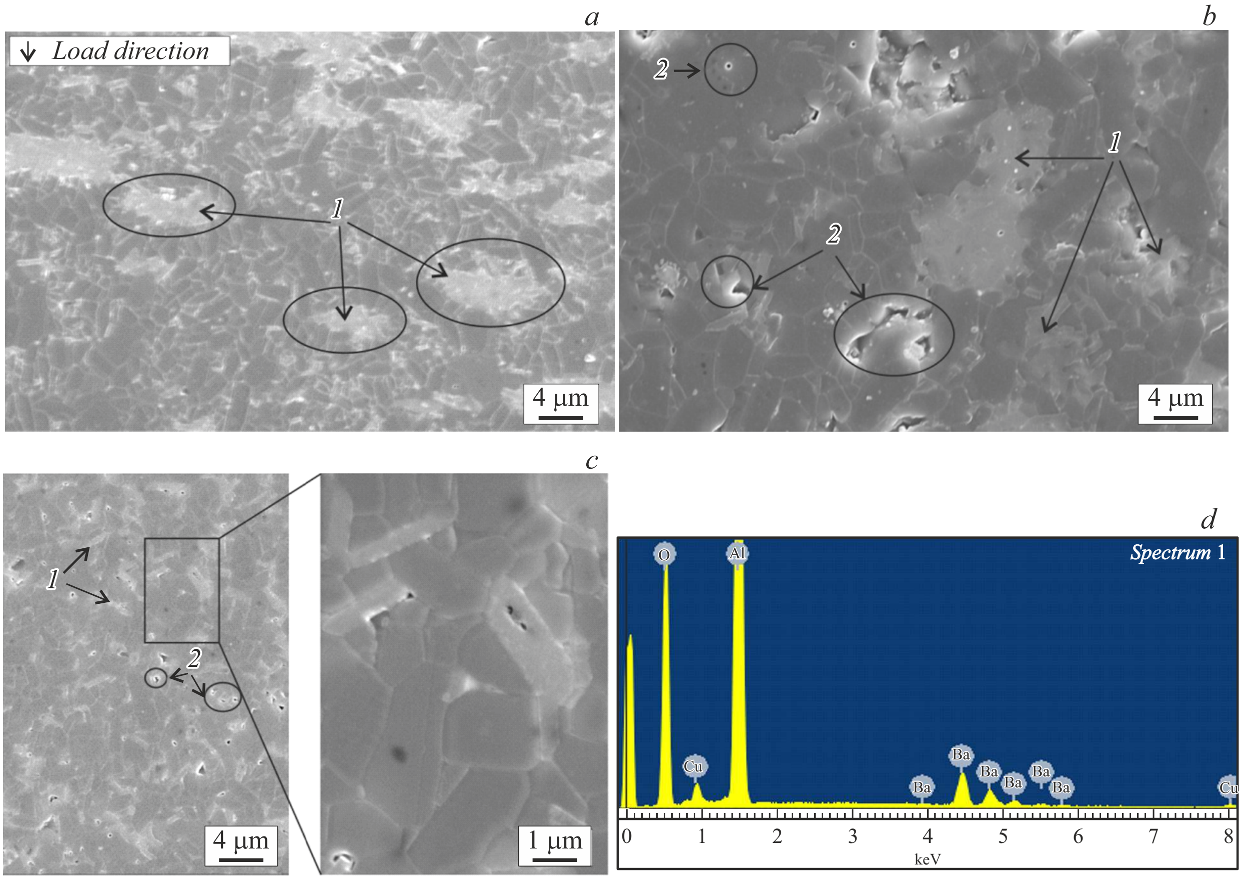

Figure 2. Structure of alumina-based composite ceramics with barium hexaaluminate prepared using different methods: *a* — hot pressing, *b* — spark plasma sintering, and *c* — pressureless sintering; *d* — electron probe microanalysis data for the region of clusters of light platelets. *1* — Barium hexaaluminate platelets; *2* — pores.

the larger size of alumina grains. This explains why the material has a higher open porosity than the ones obtained by pressureless sintering and hot pressing.

The composites prepared by pressureless sintering and hot pressing have the same critical stress intensity factors: $5.7 \pm 0.1 \mathrm{MPa} \cdot \mathrm{m}^{1/2}$. Such values are considered high for alumina-based ceramics [8]. Since the structures of materials differ, the reasons behind their high fracture toughness should also be different. In the material obtained by pressureless sintering, it is probably attributable to the uniform distribution of barium hexaaluminate platelets and various mechanisms for fracture toughness enhancement, including deflection of the crack growth path and platelet bypassing and destruction (Fig. 3). Particularly noticeable is the mechanism of crack growth path deflection, which is considered to be one of the most efficient in enhancing the fracture toughness, but is not necessarily manifested in all materials [9]. An example of its implementation is highlighted by ovals in Fig. 3, *a*. At the same time, this material has the lowest hardness, which may also be attributed to the influence of barium hexaaluminate and the presence of a large number of pores. The

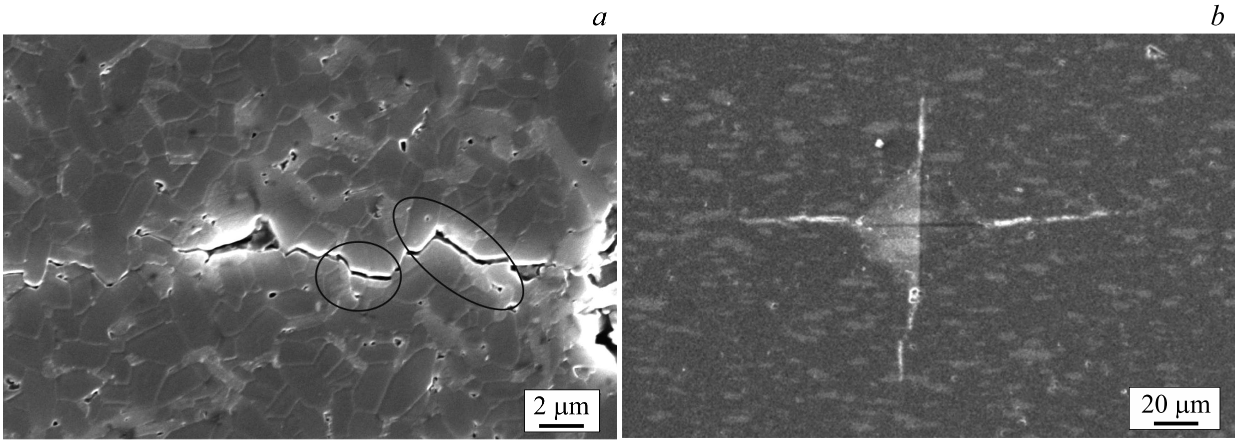

Figure 3. *a* — Magnified image of crack propagation in the material obtained by pressureless sintering; *b* - indentation in the material obtained by hot pressing.

material obtained by spark plasma sintering has the highest hardness.

In the material obtained by hot pressing, cracks stop in the regions of accumulation of barium hexaaluminate platelets. In this case, a composite material reinforced by clusters of barium hexaaluminate platelets with a certain predominant orientation was formed. A material with such a structure has a limited scope of application, since its properties may vary with its orientation relative to the direction of application of the load. Thus, according to the results of microscopic imaging (Fig. 3, *b*), a crack propagating in the direction transverse to the barium hexaaluminate platelets gets „stuck" and is halted in light regions. When cracks propagate in the longitudinal direction, barium hexaaluminate grains present no obstacle to this. It should be noted that cracks propagating in the transverse direction are shorter.

Thus, the conducted comparative study of the influence of different sintering techniques on the structure and properties of alumina–barium hexaaluminate composites revealed a number of characteristic features. Clusters of platelets oriented transversely to the direction of applied load form in the process of hot pressing. In the case of spark plasma sintering, the orientation of barium hexaaluminate grains in the composite does not depend on the direction of load application. The materials obtained by pressureless sintering and hot pressing have the highest fracture toughness. The critical stress intensity factor is $5.7\,\mathrm{MPa}\cdot\mathrm{m}^{1/2}$ for both materials. In the composite obtained by pressureless sintering, this is attributable to the formation of a structure with uniformly distributed prismatic grains of barium hexaaluminate and the implementation of various mechanisms for fracture toughness enhancement, such as platelet bypassing and destruction and deflection of the crack growth path. This material holds the most promise for industrial applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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