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Differences in the sintering mechanisms of α - and γ -Al₂O₃ nanopowders after addition of Bi₂O₃

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In this work, we experimentally studied the sintering of compacts of the composition α -Al₂O₃ (96 mol.%)+Bi₂O₃ (4 mol.%) and γ -Al₂O₃ (96 mol.%)+Bi₂O₃ (4 mol.%) obtained by cold isostatic pressing at a pressure of 1 GPa. Depending on the type of Al₂O₃ crystal lattice, a significant difference was found in the nature of sintering and the final composition. A nonmonotonic nature of shrinkage during sintering of α -Al₂O₃ with Bi₂O₃ around 1100°C has been established.

Keywords: aluminum oxide, bismuth oxide, crystal structure, sintering, cold isostatic pressing.

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The use of compositions suitable for liquid-phase sintering is one of the most efficient methods for reducing the sintering temperature of ceramics. However, the chemical and temperature stability of Al₂O₃ restricts severely the choice of alloying additives that could potentially reduce the sintering temperature [1] or even enable liquid-phase sintering.

The Al₂O₃–Bi₂O₃ system is worthy of interest due to its low melting point (the eutectic temperature is 820°C in Bi₂Al₄O₉–Bi₂O₃, and the peritectic temperature is 1070°C with Bi₂Al₄O₉ decomposition [2]) and, consequently, the possibility of liquid-phase sintering of a corundum ceramic material. The specific features of sintering of such compositions are poorly investigated.

One probable reason why this system remains understudied consists in the fact that its eutectic temperatures are much lower than the traditional sintering temperatures of corundum ceramics at which MgO, MnO, SiO₂, ZrO₂, and TiO₂ additives [1,3–5] have been well proven over the years and are more efficient. However, a surge in interest in the production of ceramics from nanopowders prone to sintering at significantly lower temperatures [6] necessitates the search for lower-melting additives.

The aim of the present study is to examine the specifics of sintering of compacts prepared by cold isostatic pressing (1 GPa) of α - and γ -Al₂O₃ nanopowders with added Bi₂O₃ (4 mol.%).

Aluminum oxide was produced by chemical precipitation of aluminum sulphate Al₂(SO₄)₃ · 18H₂O by an ammonia solution with subsequent calcination for water removal and particle growth. The calcination temperature for γ -Al₂O₃ synthesis was 900°C (2 h). In order to increase the particle size and also perform the γ -Al₂O₃ → α -Al₂O₃ transformation, a fraction of powder was calcinated addi-

tionally at 1000°C. A planetary mill with corundum grinding bodies was used for mixing with Bi₂O₃ in an aqueous medium.

The size distribution of particles was determined using a JEM-200A transmission electron microscope. The structure of obtained samples was studied with a JSM-6490LV scanning electron microscope. X-ray diffraction analysis was performed using a DRON-3 setup (filtered CuK α - radiation). Shrinkage during sintering was monitored with a DIL 402 PC dilatometer.

Figure 1 presents the shrinkage curves of compacts of the initial α -Al₂O₃ and γ -Al₂O₃ nanopowders with particle sizes of 50 and 10 nm, respectively, and compacts of these powders with the addition of 4 mol.% Bi₂O₃.

The shrinkage onset temperature (t_1) for γ -Al₂O₃ is 800°C, being lower than the one for α -Al₂O₃ (920°C). The pattern of sintering was altered when 4 mol.% Bi₂O₃ were added to the composition. The shrinkage onset temperature of γ -Al₂O₃–Bi₂O₃ decreases to 700°C, but the shrinkage process slows down above 1130°C (t_2). The mixing of Bi₂O₃ with nanopowder α -Al₂O₃ resulted in different alterations of the shrinkage curve: the initial stage of shrinkage remains unchanged, but the sample size starts increasing above 1100°C, reaching its maximum at 1125°C (t_3). This expansion could be associated with the formation of bismuth aluminate. To test this assumption, samples of both compositions were pressed isostatically under 1 GPa and sintered with isothermal processing at a temperature close to the peak one (1150°C, 10 h). Samples were then cooled rapidly to room temperature in order to preserve the high-temperature composition, but X-ray analysis showed no signs of the formation of a new phase (Fig. 2). However, a different regular pattern was revealed: Bi₂O₃-related peaks vanished from the spectra for α -Al₂O₃–Bi₂O₃ after sintering, but remained in the γ -Al₂O₃–Bi₂O₃ system. The vanishing of Bi₂O₃ in the course of sintering is not

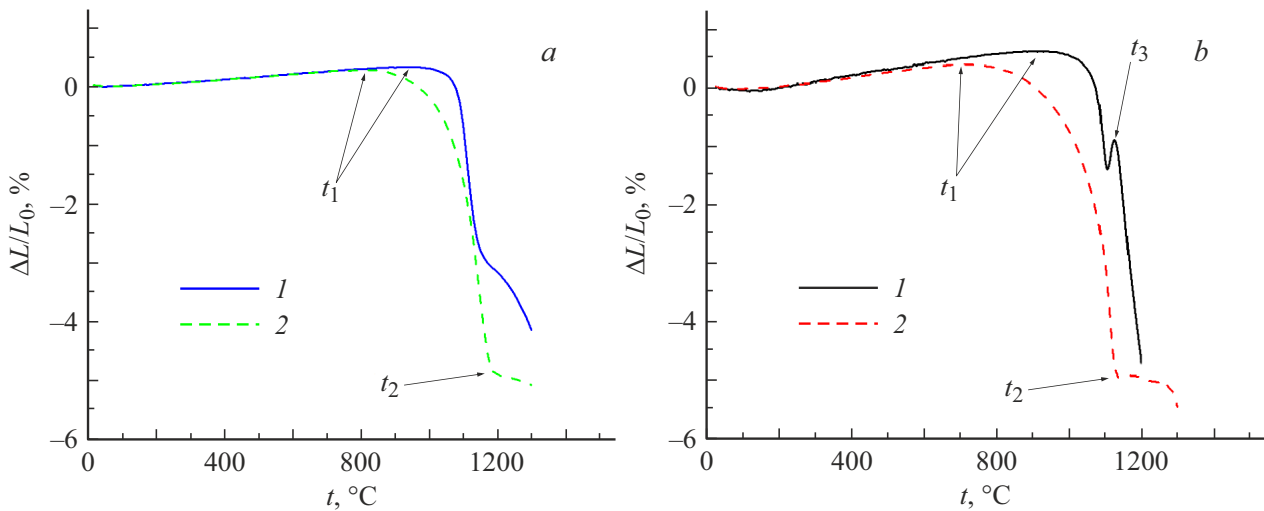


Figure 1. Results of the dilatometric study of sintering of nanopowders: *a* — α - Al_2O_3 (1) and γ - Al_2O_3 (2); *b* — α - Al_2O_3 + 4 mol.% Bi_2O_3 (1) and γ - Al_2O_3 + 4 mol.% Bi_2O_3 (2). The temperature growth rate was $4^\circ\text{C}/\text{min}$.

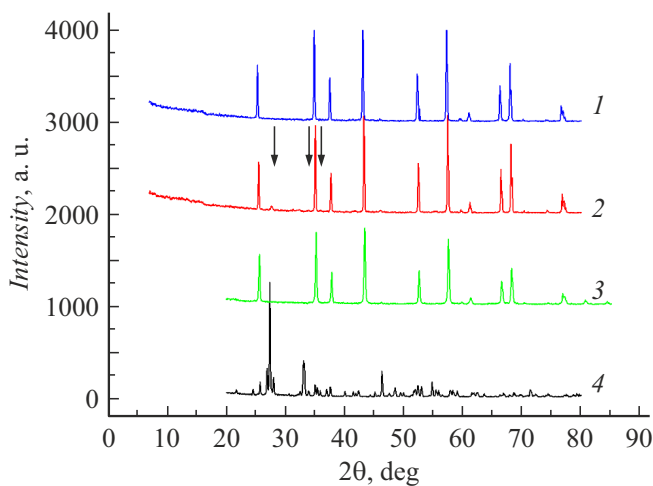


Figure 2. Diffraction patterns after sintering of compacts α - Al_2O_3 + 4 mol.% Bi_2O_3 (1), γ - Al_2O_3 + 4 mol.% Bi_2O_3 (2), and initial α - Al_2O_3 (3) and Bi_2O_3 (4). Arrows denote the Bi_2O_3 reflections retained after sintering.

unexpected, since it tends to evaporate at high temperatures; however, the selectivity of this process (i.e., dependence on the crystal structure of Al_2O_3 with which bismuth oxide is sintered) is conspicuous.

It should be noted that the formation of bismuth aluminate under the chosen thermal processing conditions was not identified by X-ray diffraction. According to the equilibrium diagram [2], this compound is produced under equilibrium conditions in the process of melt cooling.

It can be seen from Fig. 3 that the microstructure of samples after dilatometric studies is characterized by a fairly high porosity, which is attributable both to moderate temperature levels and the lack of long isothermal exposures.

Densities of samples before and after sintering

Composition of samples	Density ρ , g/cm^3	
	Initial compacts	After sintering (1150°C, 10 h)
γ - Al_2O_3	1.65	1.94
α - Al_2O_3	1.83	2.03
γ - Al_2O_3 + 4 mol.% Bi_2O_3	1.70	1.98
α - Al_2O_3 + 4 mol.% Bi_2O_3	1.79	2.06

At this sintering stage, the γ - Al_2O_3 nanopowder yields a structure with coarser grains (Fig. 3, *a*). The presence of brighter Bi_2O_3 inclusions, which are not seen in the image of the sample prepared from the α - Al_2O_3 powder (Fig. 3, *b*), is also evident.

The densities of samples, which were determined using the geometric method, are listed in the table.

The obtained results reveal a significant difference between the processes occurring in the course of sintering of Al_2O_3 - Bi_2O_3 nanopowders with different crystal lattices of aluminum oxide in the system. It was found that difficulties arising in sintering of nanopowders in the α - Al_2O_3 - Bi_2O_3 system are attributable to an abrupt expansion of samples following the onset of shrinkage. This problem is erased if one uses nanopowder γ - Al_2O_3 instead of α - Al_2O_3 . The vanishing of Bi_2O_3 after calcination of α - Al_2O_3 compacts with 4 mol.% Bi_2O_3 at 1400°C was also detected. This may be attributed to the elevated volatility of bismuth oxide. At the same time, γ - Al_2O_3 - Bi_2O_3 samples with an equivalent initial concentration of bismuth oxide retained it after thermal processing under the same conditions.

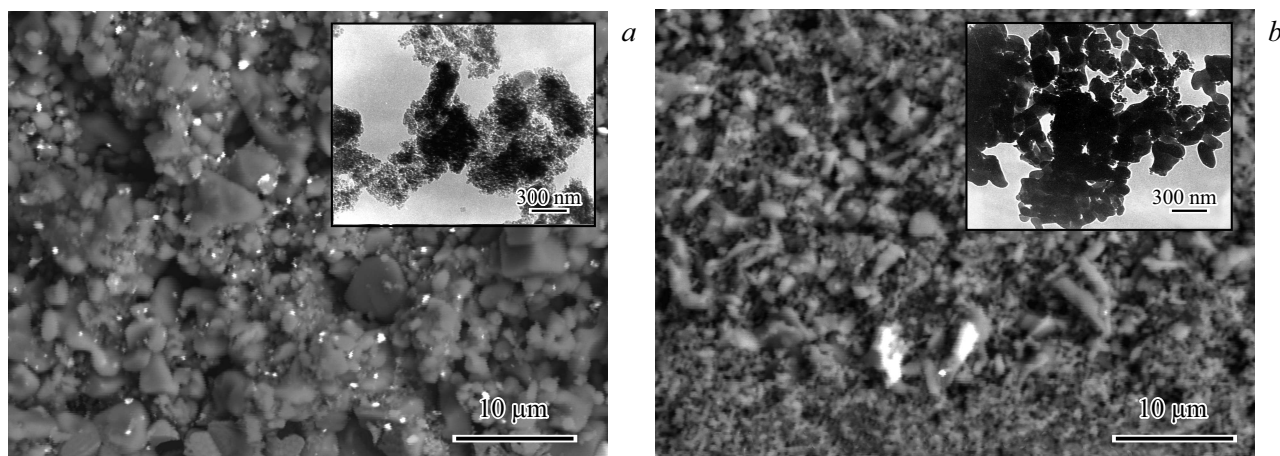


Figure 3. Microscopical images of the structure of samples γ - Al_2O_3 + 4 mol.% Bi_2O_3 (a) and α - Al_2O_3 + 4 mol.% Bi_2O_3 (b) after thermal processing at 1300°C. The structures of initial Al_2O_3 nanopowders are shown in the insets.

Conflict of interest

The authors declare that they have no conflict of interest.

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