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Nanopowders and Dense Nanostructural Ceramics of α -Al₂O₃

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Abstract

Three different nanopowders of α -Al₂O₃ were characterized. Their behaviour under dry uniaxial compacting and agglomeration in the air without applying any external pressure was investigated. Ceramics which is 99 % dense was obtained at agglomeration temperature of 1300 °C; its grain size was about 200 nm. It was established that for low-temperature agglomeration it is reasonable to use the powder containing aggregates that are conserved during filling the press mold at the initial period of pressure rise but get destroyed at subsequent stages of compacting. It was demonstrated that the optimal method of molding makes it possible to obtain dense ceramic material even at 1150 °C with the conservation of grain size at a level of 100 nm and less.

Key words: aluminium oxide, nanopowder, agglomeration, nanoceramics

INTRODUCTION

Aluminium oxide is one of the most promising ceramic materials for a broad range of applications under extreme performance conditions due to the combination of high hardness, thermal stability, chemical inertness, on the one hand, and availability with cost-effectiveness on the other hand. However, widespread ceramic materials on the basis of Al₂O₃ with macrocrystalline structure (with crystallites 5–10 μ m in size) are characterized by fragility, low crack growth resistance (3–4.5 MPa · m^{0.5}) and high sensitivity to erosion and abrasion, which limits their application.

A fundamental reason of the low strength of materials based on Al₂O₃ is anisotropy of thermomechanical characteristics of the crystal of stable α -modification which is characterized by the hexagonal structure of the unit cell. During the formation of the material through high-temperature agglomeration, at the stage of cooling the chaotically oriented crystals (grains) turn out to be nonconforming in the coefficients of thermal expansion with the neighbours having a different orientation. This causes the generation of intergrain microstrain,

which is proportional to grain size. In this situation, microstrain turns out to be so high in the macrocrystalline ceramics that it causes the formation of microcracks, which causes a substantial decrease in the strength of the material.

Solution of the goal to increase the strength of materials based on Al₂O₃ is at present expected to be connected with a decrease in technological microstrain by conserving the grain size in the nanometer scale.

It was shown previously [1, 2] that a multiple elevation of wear resistance of the ceramics based on Al₂O₃ can be achieved due to the development of a material with fine uniform structure possessing the limiting density. For a given phase composition, it is important to synthesize the material with the least nanometre scale of the structure, with high uniformity, minimal porosity and well formed boundaries between the crystallites [3, 4]. As a rule, fulfilling these conditions one can obtain a ceramic material with grain size below 200–300 nm, having the crack growth resistance above 7 MPa · m^{0.5} and hardness above 20 GPa.

Nevertheless, in spite of increasing interest to obtaining nanostructured ceramic oxide

materials [5–10], there are only few successful works dealing with ceramic nanostructural materials based on aluminium oxide. This may be connected with the difficulties connected with the preparation of initial nanopowder of α - Al_2O_3 , which is confirmed by its almost complete absence in the market.

Some attempts to use the gamma phase as the initial material, in spite of the complicating effect of the phase transition into the stable modification during heating the blank, achieved relative success. However, the use of rather complicated methods of hot pressing, spark plasma-enhanced agglomeration, magnetopulse pressing restricted the possibilities of the practical implementation of this approach [11–14].

There is a small number of publications the authors of which succeeded in obtaining α - Al_2O_3 powder on the laboratory scale [15–22]. However, it is likely that only the authors of two works [23, 24] succeeded in sintering the synthesized powder to obtain relatively dense (3.76 and 3.80 g/cm³, respectively) ceramics with the conservation of grain size in the nanometer range. The indicated procedures seem unlikely to win widespread application because the authors of [23] achieved the result only after separating about 20 % of the finest fraction from the synthesized powder with the help of centrifuging, while the authors of [24] achieved the result through crystallization from aluminium hydroxide gel doped with acrylamide, with the large ratio of the polymer to the product, followed by pressing at too high pressure (~1.5 GPa).

The goal of the work was to study the possibility to obtain dense nanostructural materials based on commercially available nanopowders of α - Al_2O_3 using thermal agglomeration without hot pressing or spark plasma-enhanced agglomeration.

EXPERIMENTAL

Three kinds of α - Al_2O_3 powder synthesized in Nanokompozit Co Ltd. (Novosibirsk) were used in the work [25]. Two of them, SI-1 and SI-2, were prepared by superfine grinding in planetary mills with different intensities of action, followed by the removal of the material

worn from milling bodies with the help of acid treatment [20]. One more powder (STK) was synthesized by crystallization of the gel containing 3 % of seeding α - Al_2O_3 nanopowder [16]. X-ray phase analysis of powders and agglomerated materials was performed with the X-ray diffractometer DRON-4 ($\text{CuK}_{\alpha 1}$ -radiation) with graphite monochromator. The size of crystallites in powders and grains in agglomerated materials was determined using PowderCell 2.4 programe with compulsory input of the parameters of standard samples recorded under identical conditions. The results were controlled periodically by subtracting the instrumental broadening from sample lines by means of function sweep using Microcal Origin 7.0 software, followed by determination of size through solving the system of nonlinear equations. The specific surface of powder samples was determined with the help of Sorbtometr set-up by means of thermal desorption of nitrogen. Chemical analysis was performed by means of laser ionization mass spectrometry with Emal-2 instrument (Russia) and/or by complete dissolution of samples followed by element determination with an Agilent 7500a ICP-MS.

To carry out granulometric and electron microscopic analyses of powder samples, water suspensions were prepared. For this purpose, a weighed portion of powder was put into a diluted solution of HNO_3 (pH 3–4), and the suspension was treated with ultrasonic dispersant UD-11. Determination of the granulometric composition was carried out with the help of laser Doppler granulometer and anemometer LAD-079 (Russia) and/or NICOMPTM 380 ZLS granulometer (USA). Electron microscopic analysis was performed using the transmission electron microscopy JEM2000FX2. The analysis of the nanostructure of agglomerated samples was made with the help of scanning electron microscopes TM-1000 and EX-23000BU.

TABLE 1

Content of major impurities in Al_2O_3 powder, mass %

| Powders | Si | Fe | Cr | Mn |
|---------|--------------------|--------------------|--------------------|--------------------|
| SI-1 | 0.4 | 1.5 | 0.4 | 0.1 |
| SI-2 | 0.01 | 0.15 | 0.06 | 0.02 |
| STK | $<1 \cdot 10^{-3}$ | $<1 \cdot 10^{-2}$ | $<1 \cdot 10^{-3}$ | $<1 \cdot 10^{-3}$ |

TABLE 2

Phase composition and size characteristics of powders under investigation

| Powders | Content of α -Al ₂ O ₃ , % | Crystallite size, nm | S_{sp} , m ² /g | Average size, measured by laser light scattering, nm | Pycnometric density, g/cm ³ |
|---------|---|----------------------|------------------------------|--|--|
| SI-1 | 100 | 20 | 42 | 20–25 | 3.4 |
| SI-2 | 100 | 40 | 36 | 56 | 3.8 |
| STK | 100 | 50 | 33 | 53 | 3.6 |

Powders were subjected to dry uniaxial pressing in a steel matrix. In some cases powder disaggregation was carried out by means of treatment in acetone using the planetary mill AGO-2M at the acceleration of 6–10g. Milling balls and cylinders were made of Al₂O₃ or ZrO₂. Powder agglomeration in the air was performed at the heating rate of 5 °C/min, followed by isothermal exposure for 1.5 h. The density of raw and agglomerated materials was determined using Archimedean procedure according to State Standard GOST 20018–74.

RESULTS AND DISCUSSION

Characterization of initial powders

The characteristics of initial powders obtained through examination are listed in Tables 1 and 2.

The curves of particle size distribution for SI-1 and SI-2 powders are shown in Fig. 1, while Figs. 2–4 show the electron microscopy images of SI-1 and STK powders. One can see that all the three kinds of powder are indeed nanopowders, SI-1 containing also a definite fraction of larger particles that may be aggregates. The results of the comparative analysis of the data on the size of SI-1 crystallite size and the data on particle size calculated on the basis of specific surface values (36 nm) also provide evidence of strong aggregation of the powder. Quite contrary, SI-2 and STK powders are likely to be weakly aggregated because the ultrasonic treatment of the suspension causes their almost complete disaggregation. This is also confirmed by the fact that the data obtained on the size of crystallites are in good agreement with the data calculated on the basis of specific surface values.

Powder molding

The curves of powder pressing are shown in Fig. 5. The powders obtained by intense grinding demonstrate much higher compactability than the powder synthesized from gel. Taking into account the fact that the particle sizes in SI-1 and STK powders are approximately the same, evident difference in moldability may arise only in the case if the dry SI-1 powder is

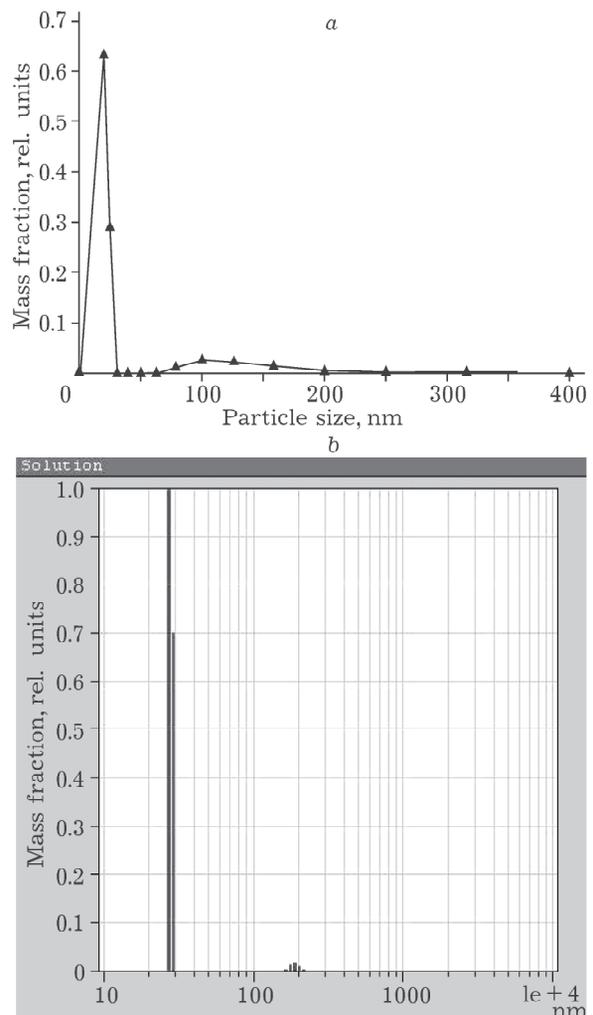


Fig. 1. Particle size distribution in SI-1 (a) and SI-2 (b) powders.

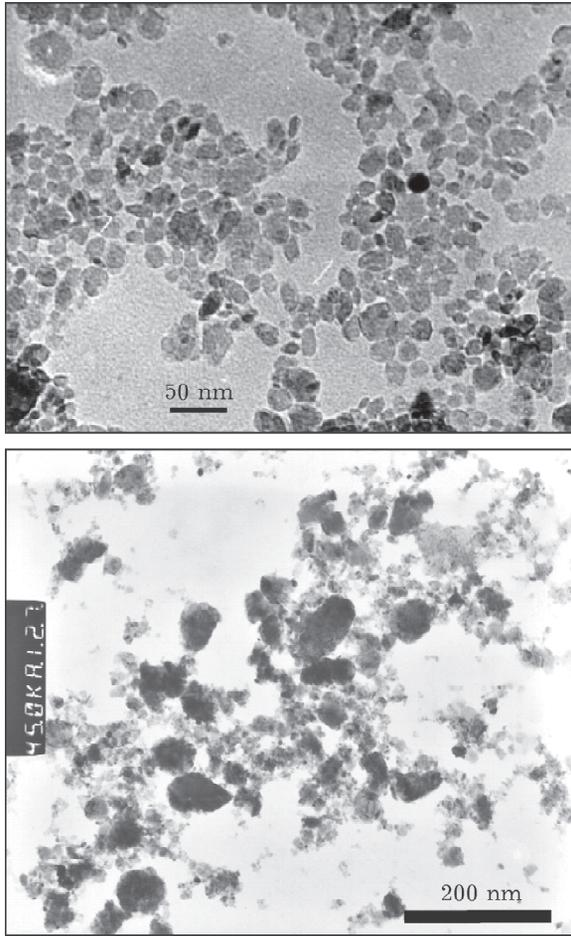


Fig. 2. TEM photomicrographs of SI-1 powder.

composed of agglomerates, the strength of which is sufficient to prevent from destruction during filling the press mold and conserve integrity at the initial stage of pressure rise. With further increase in compacting pressure, the strain starts to exceed the breaking point of agglomerates, and the particle packing becomes even denser. The agglomerates comprising STK powder are likely to be not strong, so it is impossible to achieve their tight packing before the start of destruction. With the destruction of aggregates and consequent increase in the area of contact between the moving particles, the friction between particles increases sharply, which does not allow one to achieve high density. As expected, disaggregation of STK powder in acetone decreases its compactability even more. It should be noted that the use of cold isostatic pressing does not lead to an increase in the density of the raw blank but during subsequent sintering the samples clearly

exhibit concave lenses. This is an evidence of the non-uniform distribution of density over the volume of the raw blank and insufficient degree of pressing of the central part. In the case when the applied external pressure is compensated by the forces of friction between particles in the outer layers of sample, it is exactly this picture that must be observed.

Difference in the strength of agglomerates for different powders can be easily explained if we take into account the fact that the last stage of obtaining SI powders is trituration of clumps formed during drying water suspen-

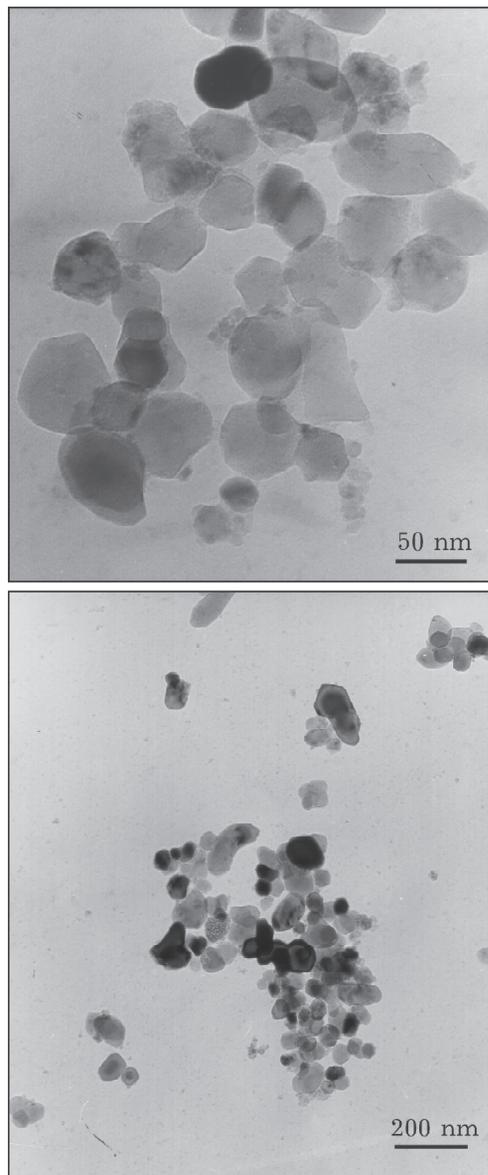


Fig. 3. TEM photomicrographs of STK powder.

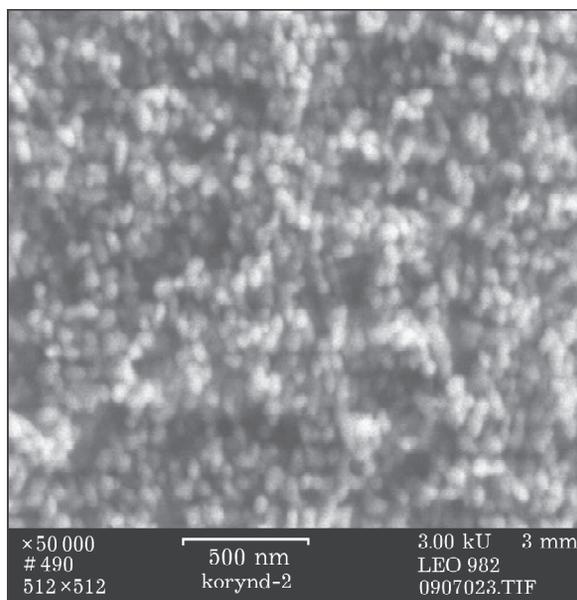


Fig. 4. SEM photomicrographs of STK powder.

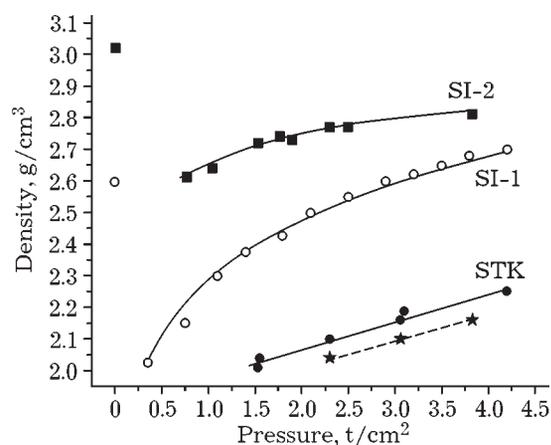


Fig. 5. Density of raw blank depending on the pressure applied. Asterisks show the points for disaggregated STK powder.

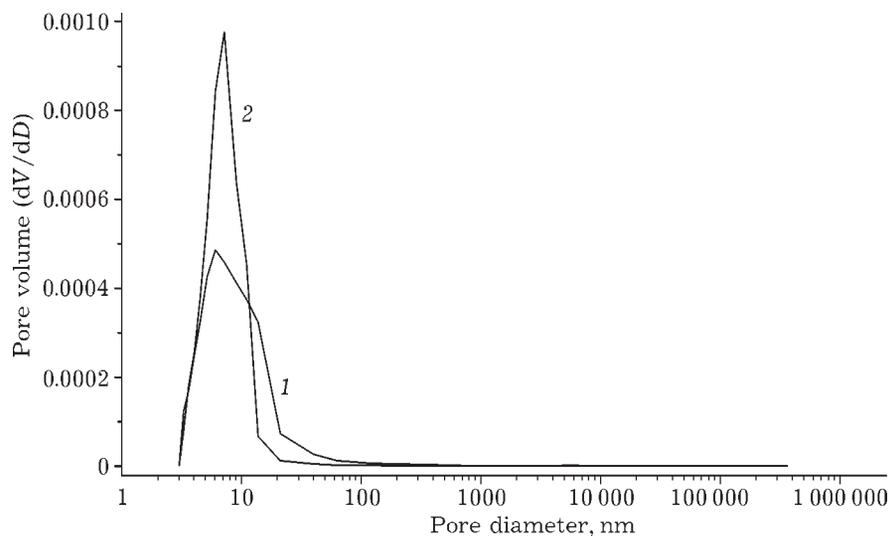


Fig. 6. Pore size distribution in powders pressed at a pressure of 1 t/cm² (1) and deposited from suspension (2).

sions, while for STK powder, the dry powder formed during gel annealing is triturated. With the removal of surface hydroxyl groups, the formed oxygen bridges (Al-OH + OH-Al → Al-O-Al + H₂O) bind neighbouring particles with each other rendering strength to the agglomerates of SI-2 powder. At the same time, while measuring the granulometric composition in acidic water suspension, oxygen bridges are attacked by protons and get destroyed easily.

Aggregation of SI-1 powder (see Figs. 1, a and 2) most probably has a different nature. Agglomerates are formed as a result of intense mechanical action during grinding and are not destroyed during trituration or pressing.

It is interesting to investigate the points (see Fig. 5) corresponding to zero pressure. These samples were obtained by deposition in the field of gravitation forces from aqueous suspensions similar to those used for granulometric and electron microscopic studies. An even layer 3–4 mm thick is formed at the bottom of the glass. When drying this layer gets cracked. Nevertheless, in the case of slow drying defect-free fragments with the area up to 7–8 cm² are formed. The density of such a sample for SI-2 powder turned out to be extremely high; it accounts for 75 % of the theoretically possible value (3.987 g/cm³) for α -Al₂O₃. It is known that in the case of the closest packing of spherical particles the density reaches 74 %. In this connection, it may be assumed that perfect packing of the particles is formed during the deposition of the suspension.

Pore size distribution for this sample and for the sample of the same powder pressed under the pressure of 1.05 t/cm² is presented in Fig. 6. One can see that the deposited sample has a very narrow pore size distribution with the average size of 8–10 nm, which almost precisely corresponds to the diameter of cavities in the closest packing of spherical particles with a size of 40 nm. For SI-1 powder having the bimodal particle size distribution, this could not be achieved.

The obtained result is very interesting from the viewpoint of the evaluation of potential possibilities to obtain very dense nanoceramics of SI-2 powder because it allows us to estimate its potential when choosing the optimal method and molding conditions.

Agglomeration

Results of agglomeration of samples pressed from powders at a temperature of 1300 and 1450 °C (Fig. 7) agree with generally accepted notions about agglomeration of the samples pressed from nanopowders [9, 10]. SI-2 sample composed of well-packed nanoparticles reaches high density values even at 1300 °C. The closer is particle packing in mold, the higher is the density of agglomerated material, which reached 98–99 % even at this temperature. The microstructure of this material (Fig. 8) allows us to relate it to nanostructural materials un-

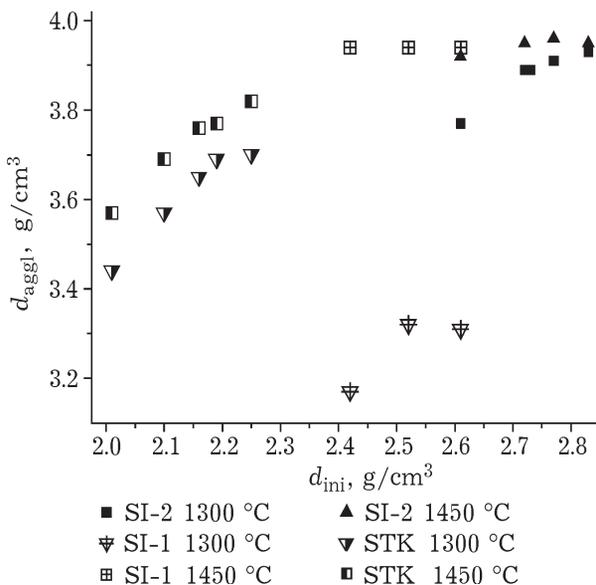


Fig. 7. Density of the agglomerated oxide (d_{aggl}) depending on the density of initial sample (d_{ini}) at different temperatures.

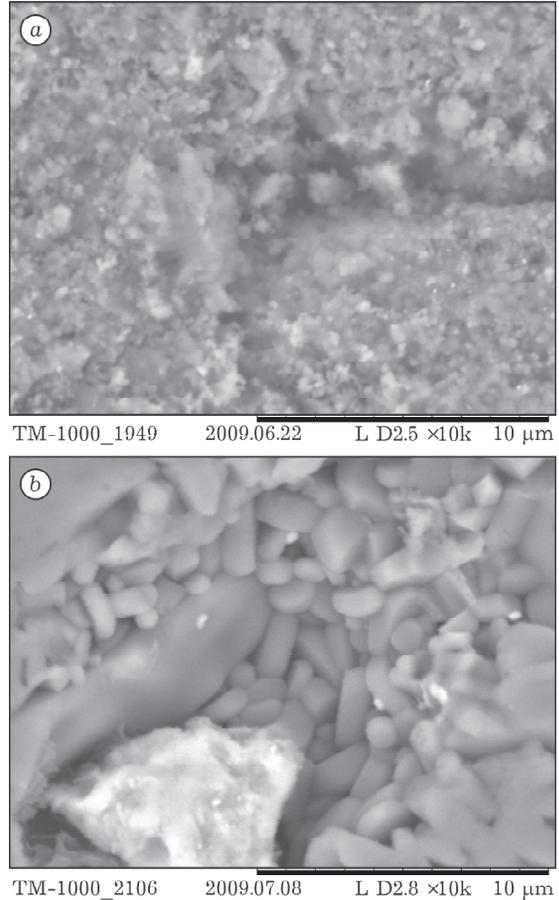


Fig. 8. SEM photomicrographs of the surface of contact, agglomerated at a temperature of 1300 (a) and 1450 °C (b).

ambiguously. In this situation, the grain size is so small that it cannot be determined from the profile of X-ray lines; it is equal to 180 nm. Quite contrary, the sample of aggregated powder SI-1 exhibits the effect of differential agglomeration. First of all, internal agglomeration occurs; large pores are formed between the agglomerates. Their healing requires higher temperature. As a consequence, the density of samples made of SI-1 powder, achieved at 1300 °C, is much lower than the density of the sample of SI-2 powder.

It is interesting to stress that, though the sample obtained by the deposition of the aqueous suspension of SI-1 powder has good density, it agglomerates worse than the pressed sample (3.3 and 3.7 g/cm³, respectively). This is due to the fact that before pressing the powder is triturated in a mortar and undergoes partial mechanical destruction of agglomerates, which is not observed during the formation of suspension.

At a temperature of 1450 °C the samples of both powders get agglomerated to the density of 98–99 % (see Fig. 8, b), which remains constant during subsequent temperature rise to 1600 °C.

It is necessary to stress that for the sample molded from STK powder, which we assume to contain no strong aggregates and to have not the close packing of particles, at 1300 °C much higher density is characteristic than for SI-1 sample. At the same time, at a temperature of 1450 °C its density turns out to be smaller because too large pores remaining in the pressed sample at moderate compacting pressures require higher temperatures for healing.

So, the optimal nanopowder for low-temperature agglomeration is that composed of agglomerates, with the particles providing the achievement of dense packing at the initial stage of pressing but getting destroyed at subsequent stages without the use of super-high pressure. In the case under consideration, SI-2 is the powder meeting these criteria in the best manner. On the contrary, the powder composed of strong agglomerates (for example, SI-1), in spite of good compactability, requires higher temperatures to achieve high density, but this is critical from the viewpoint of the conservation of grain size in the nanometer range (see Fig. 8). On the other hand, if the agglomerates of particles are too unstable and get destroyed during pressing even before the closest packing is achieved, the forces of friction between the particles become too large to provide compaction under moderate compacting pressure. In this case, it is reasonable to use either super-high pressure or colloid pressing procedures. In the present work this approach is applicable to the sample of STK powder.

Nevertheless, comparative analysis of the data on the density of non-agglomerated samples of SI-2 powder obtained by pressing and by deposition from suspension shows that the used pressure range is insufficient for the optimal packing of particles which is achieved by means of deposition procedure. This means that at higher pressures or using other methods of SI-2 powder molding higher density of the pressed blanks may be achieved. Therefore, lower temperature will be necessary for agglomeration. The data on the agglomeration of the samples obtained by deposition are

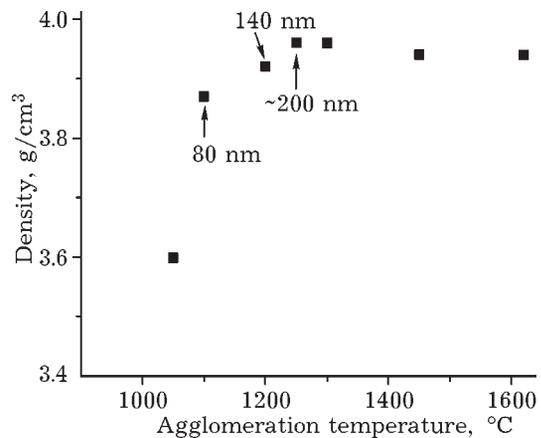


Fig. 9. Dependence of the density of agglomerated aluminium oxide sample, compacted by deposition, on agglomeration temperature.

presented in Fig. 9. One can see that using a suitable method of molding SI-2 powder one may obtain almost pore-free ceramics even at 1100–1150 °C. The grain size is 100 nm and smaller, which is confirmed by the data of electron microscopic and X-ray studies.

CONCLUSIONS

1. The behaviour of three commercially available nanopowders of α -Al₂O₃ with particle size 20, 40 and 50 nm during agglomeration was studied. The powder with particle size 50 nm composed of the aggregates of medium strength providing the achievement of the closest packing of particles at the initial stage of packing but getting destroyed at subsequent stages is preferable for obtaining pore-free ceramics. When using the powder composed of stronger aggregates, it is necessary to use higher temperatures to obtain dense ceramics, in spite of substantially smaller particle size; the powder with weak aggregates cannot be pressed due to large friction forces between the particles.

2. By means of dry uniaxial pressing and agglomeration in the air without applying external pressure, we obtained 99 % dense ceramics of α -Al₂O₃ with grain size about 200 nm. So, it is possible to obtain dense nanostructural ceramics also without using expensive methods of hot pressing or spark plasma-enhanced agglomeration.

3. It was shown that using the optimal method of powder molding for the powder with

particle size 30 nm, it is possible to obtain dense ceramic material at 1150 °C with the conservation of grain size at a level of 100 nm and less.

REFERENCES

- 1 D. Sherman D., D. Brandon, *Adv. Eng. Mater.*, 1, 3–4 (1999) 161.
- 2 B. Kerkwijk, E. Mulder, H. Verweij, *Adv. Eng. Mater.*, 1, 1 (1999) 69.
- 3 M. Yu. Gutkin, I. A. Ovidko, *Usp. mekhaniki*, 1 (2003) 68.
- 4 A. I. Gusev, A. A. Rempel, *Nanocrystalline Materials*, Cambridge Int. Sci. Publ., 2004. p. 351.
- 5 R. Chaim, M. Levin, A. Shlayer, C. Estournes, *Adv. Appl. Ceramics*, 107, 3 (2008) 159.
- 6 A. V. Ragulya, *Adv. Appl. Ceramics*, 107, 3 (2008) 118.
- 7 A. P. Hynes, R. H. Doremus, R. W. Siegel, *J. Am. Ceram. Soc.*, 85, 8 (2002) 1979.
- 8 G. R. Groza, *Int. J. Powder Metallurgy*, 35, 7 (1999) 59.
- 9 M. J. Mayo, *Mater. and Design*, 14,6 (1993) 323.
- 10 P. Bowen, C. Carry, *Powder Technol.*, 128 (2002) 248.
- 11 S.-C. Liao, Y.-J. Chen, B. H. Kear, W. E. Mayo, *NanoStructured Mater.*, 10, 6 (1998) 1063.
- 12 R. S. Mishra, C. E. Leshner, A. K. Makherjee, *Mater. Sci. Forum*, 225–227 (1996) 617.
- 13 R. S. Mishra, S. H. Risbud, A. K. Makherjee, *J. Mater. Res.*, 13, 1 (1998) 86.
- 14 V. V. Ivanov, S. N. Paranin, V. R. Khrustov, *Phys. Metals Metallography*, 94 (2002) 98.
- 15 A. Krell, H. Ma, *Nanostruct. Mater.*, 11, 8 (1999) 1141.
- 16 G. R. Karagedov, *Ceramics-Processing, Reliability, Tribology and Wear*, in G. Muller (Ed.), Weinheim, Wiley VCH, 2000, pp. 63–68.
- 17 J. Guang, X. Sun, *Acta Materialia*, 48 (2000) 3103.
- 18 R. N. Das, A. Bandyopadhyay, S. Bose, *J. Am. Ceram. Soc.*, 84, 10 (2001) 2421.
- 19 R. K. Pati, J. C. Ray, P. Pramanik, *J. Am. Ceram. Soc.*, 84, 12 (2001) 2849.
- 20 G. R. Karagedov, N. Z. Lyakhov, *KONA Powder and Particle*, 21 (2003) 76.
- 21 H. J. Goodshaw, J. S. Forrester, G. J. Suaning, E. H. Kisi, *J. Mater. Sci.*, 42 (2007) 337.
- 22 J. S. Forrester, H. J. Goodshaw, E. H. Kisi, G. J. Suaning, J. S. Zobec, *J. Austr. Ceram. Soc.*, 44, 1 (2008) 47.
- 23 G. R. Karagedov, N. Z. Lyakhov, *NanoStructured Mater.*, 11 (1999) 559.
- 24 J. Li, Y. Ye, *J. Am. Ceram. Soc.*, 89, 1 (2006) 139.
- 25 URL: <http://www.nano-composite.ru/indexe.htm>