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Features of the Crystallization of Aluminohydroxide Gel Containing Mechanochemically Prepared Nanosized α-Al_2O_3 Particles

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Abstract

The introduction of α-Al_2O_3 nanoparticles into the gel formed during the hydrolysis of aluminium nitrate causes a substantial decrease in the temperature of its transition into the thermodynamically stable modification. Along with this, the higher is the concentration of seeding within the range 0.2–5 mass % is, the lower the temperature of the formation of monophase α-Al_2O_3 is. At the same time, the temperature of the phase transition into the б-modification depends on the method of introduction the seeding into the gel. This may be connected with the nonuniform distribution of nanoparticles over its volume. The use of deionised water as a solvent instead of distilled water allows one to decrease the temperature of α-Al_2O_3 formation to 500 °C. Due to the low temperature of the formation of α-phase (<950 °C), the product consists of easily destroyable granules formed by nanoparticles 45–60 nm in size. Nevertheless, samples formed from powders with a close size demonstrate different sintering ability during the low-temperature annealing in the air (1300 °C). Their densities vary within the range 67–97 % of the theoretically possible value. This is likely to be due to the fact that separate particles in granules get grown together under unfavourable conditions.

Key words: aluminium oxide, nanopowder, synthesis, mechanochemistry

INTRODUCTION

Temperatures not lower than 1200 °C are usually necessary to obtain pure α-Al_2O_3 by hydrolysis of aluminium salts followed by crystallization of aluminium hydroxide gels. This results in the formation of the coarse product, unsuitable for the use in ceramic works without additional operations, by which usually the material contamination gets usually contaminated. With the development of nanoceramic materials science, the task was put to obtain pure nanopowder of α-Al_2O_3 and decrease maximally the gel crystallization temperature.

As early as in the 1980th, the crystallization of α-Al_2O_3 was studied in the presence of various crystallization centres introduced artificially: oxides of iron, chromium and magnesium. It was established that in some cases the temperature of the complete phase transition into a form decreases. Using multiple sedimentation, employers of Alcoa Inc. succeeded in separating the fraction with the size of 0.1 μm, decreasing the temperature of the complete crystallization to 1025 °C and finally obtaining powder with the particle size of 0.1–0.4 μm. Previously [2], using mechanochemically synthesized α-Al_2O_3 powder with the particle size of about 25 nm, we succeeded in reducing the temperature of complete transformation of the gel into the product to 850–950 °C, depending on the method of seeding introduction, and obtained easily destroyable granules composed of the particles 50–60 nm in size [3]. Then, it was demonstrated that the nanopowder formed by the destruction of granules exhibits a good formability by dry pressing and gets sintered into a practically nonporous material already at

1300 °C. In this process, one succeeds in preventing the uncontrollable growth of grains and holding their size at the level of 50–150 nm [4].

Nevertheless, detailed studies of the sintering behaviour of these powders with the particle size 50–60 nm revealed poor reproducibility of results. Powders under study had the same phase and chemical composition, crystallite size and specific surface but the density of ceramics achieved at definite temperatures varied within a broad range.

The goal of the present work was to search for additional factors defining the properties of α-Al_2O_3 nanopowders obtained from aluminohydroxide gels.

EXPERIMENTAL

Initial reagents were aluminium nitrate 9-hydrate of the ch. d. a. reagent grade, concentrated aqueous solution of ammonia, os. ch. reagent grade, and nano-α-Al_2O_3 seeding prepared according to the procedure described in [5]. The size of seeding crystallites determined by means of the analysis of the profile of X-ray lines was 17–25 nm, specific surface 69–77 m^2/g, and the mass average size of particles in the aqueous suspension (pH 4, HNO_3) according to the data of laser autocorrelation spectroscopy was (90±40) nm. Distilled, deionised and technical grade water were used as solvents. Aqueous suspension containing a definite amount of α-Al_2O_3 nanopowder was added into the solution of aluminium nitrate under intense mixing, and then the calculated amount of ammonia was added dropwise from a burette (~0.7 mL/min). The resulting gel was aged for 24 h, dried in the air at 500 °C and then annealed at different temperatures (800–950 °C). The product was crushed in a mortar or treated in the planetary mill AGO-2M at the acceleration of 6–10*g* using milling balls and cylinders made of Al_2O_3 or ZrO_2; in some cases, isopropyl alcohol (technical grade), ethanol (1st grade) or acetone of ch. reagent grade were added.

Powders were subjected to dry single-axis pressing in a steel matrix at the pressure of 2.3–2.5 t/cm^2. The pressed samples were sintered in the air at the heating rate of 5 °C/min and then kept for 1.5 h at 1300 °C. Density was determined according to Archimedean method according to State Standard GOST 20018–74.

The X-ray phase analysis of powders and sintered materials was carried out using an X-ray DRON-4 diffractometer with Cu$K_{\alpha 1}$ radiation and graphite monochromator, and Brucker D8 Advance diffractometer. Determination of crystallite size in powders and grain size in sintered materials was carried out with the help of PowderCell 2.4 software with compulsory introduction of standard samples obtained under identical recording conditions. The results were controlled periodically by subtracting the instrumental broadening from sample lines by means of function sweep within Microcal Origin 7.0 and then determining the size by solving the system of nonlinear equations. The specific surface of powders was determined using Sorbtometr instrument by means of the thermal desorption of nitrogen. Chemical analysis was carried out by means of laser ionization mass spectrometry with the help of Emal-2 instrument (Russia) and/or by complete dissolution of the sample and subsequent determination of elements with an Agilent 7500a ICP-MS. Granulometric composition was studied using the laser Doppler granulometer and anemometer LAD-079 (Russia) and/or NICOMP 380 granulometer (Santa Barbara, the USA). Electron microscopic analysis was carried out using a JEM-2000 FX2 transmission electron microscope and Zeiss 1540 XB CrossBeam scanning electron microscope; the analysis of nanostructure of sintered samples was carried out with scanning electron microscopes TM-1000 and X-23000BU.

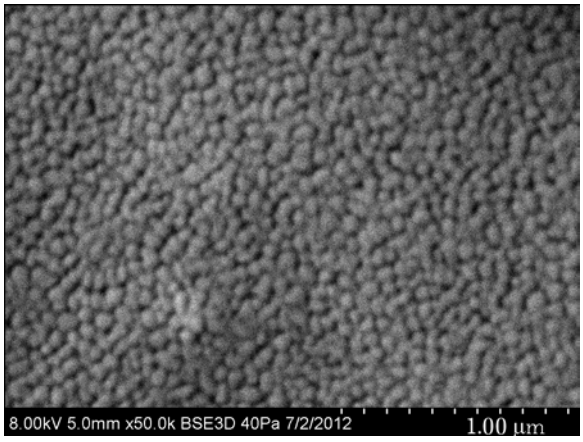

Fig. 1. Electron micrograph of sample No. 4 (see Table 1).

TABLE 1

Density of different compacts after sintering at 1300 °C

Samples	Density, g/cm^3
1	3.86
1[a]	3.48
2	3.70
3	3.70
4	3.86
4[a]	3.80
5	3.57
6	3.42
7	3.71
8	3.64

[a]Samples were obtained by simple grinding in a mortar with the addition of several drops of alcohol or acetone.

RESULTS AND DISCUSSION

We demonstrated previously [3, 4] that at the introduction of nanocorundum seeding into the solution and subsequent annealing of gel at T ~ 900 °C weakly agglomerated granules are formed; they are composed of nanoparticles of α-phase of aluminium oxide 50–60 nm in size (Fig. 1 and Table 1). After grinding under soft conditions, the granules are destroyed and nanopowder is formed (Fig. 2 and Table 1), nanopowder possesses good pressability and sintering ability. Further investigation of the transformation of ceramic nanostructure during sintering for the goal of optimization of the conditions for obtaining minimal possible grain size in the dense material showed unexpectedly that the sintering ability of nanopowders obtained at different times varies within a broad range. The data on agglomeration of samples pressed from α-Al_2O_3 powders obtained under identical conditions during the recent 3–4 years are shown in Table 1. The reproducibility of density values for the samples of one series is not lower than ±0.15 g/cm^3. The X-ray diffraction patterns of all powders correspond to α-phase, crystallite size is 45–60 nm, specific surface varies from 32 to 38 m^2/g. For each series, the dependence of density achieved at 1300 °C on the conditions of grinding of the granules formed during crystallization (dry or wet grinding, time, diameter of milling bodies, acceleration of milling bodies *etc.*) was studied.

In some cases it is rather easy to grind the powders so that the density more than 95 % of theoretically possible value (3.98 g/cm^2) is obtained at so low temperature for α-Al_2O_3 sintering, but in some cases the level of 85 % cannot be exceeded even after thorough grinding of granules. In addition, it was stressed previously [3] that after joint grinding of aluminium hydroxide with 5 % α-Al_2O_3 nanopo-

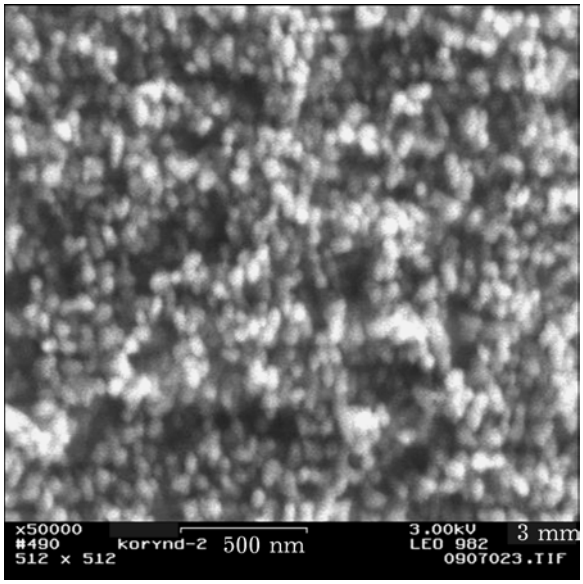

Fig. 2. Electron micrograph of sample No. 1 (see Table 1).

TABLE 2

Chemical composition of the synthesized aluminium oxide after annealing at 930 °C

Elements	Mass concentration, 10^{-3} %
C	10
N	30
Na	40
Mg	2
Si	40
K	3
Ca	5
Ti	<1
Cr	6
Mn	0.2
Fe	0.5
Ni	<0.2
Cu	<0.2
Sr	2
Y	4
Zr	70

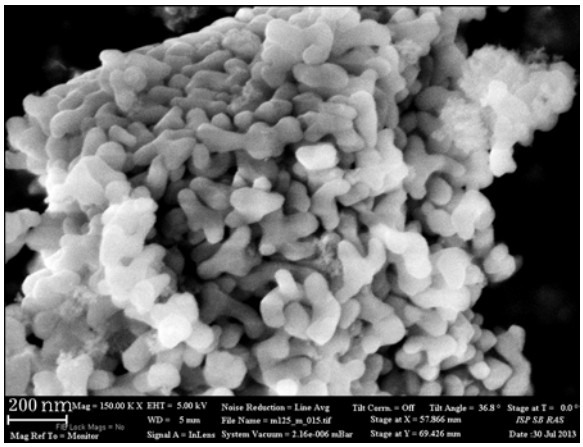

Fig. 3. Electron micrograph of sample No. 8 (see Table 1).

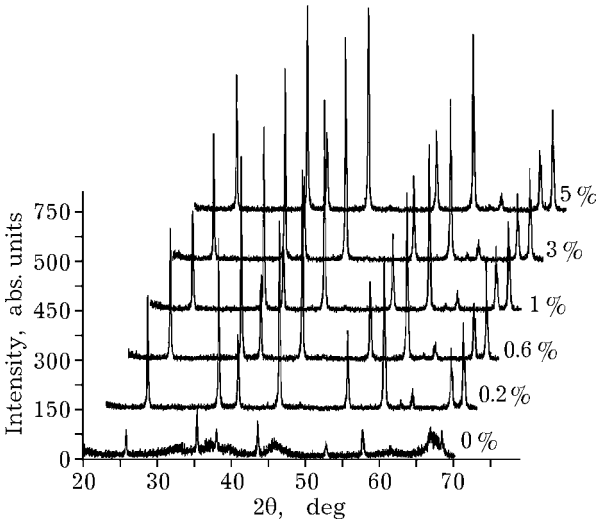

Fig. 5. X-ray diffraction patterns of synthesized samples with different seeding content (0–5 %) after annealing at 930 °C.

wder in a planetary mill, a precursor is formed, which is completely transformed at the heating temperature of 800 °C into α-modification with crystallite size 50 nm, similarly to the samples listed in Table 1. It turned out that after pressing and sintering of this nanopowder under identical conditions its density does not exceed 67 % of the theoretical value.

The chemical composition of the samples of synthesized aluminium oxide is approximately the same because the same initial substances and identical procedures were used in all the cases (Table 2). Therefore, in this case the phase composition, crystallite size and specific surface comprise far from the complete list of parameters for the evaluation of properties of nanopowder and possibilities to use it in the production of ceramics.

One can see in the micrograph of sample No. 8 (Fig. 3) possessing the unsatisfactory sintering ability that, unlike for sample No. 4 (see Fig. 1) separate particles grew together. In addition, fluffy regions corresponding to the residues of metastable aluminium oxide phases are distinguished, though diffraction patterns (Fig. 4) point to almost complete transition into the α-phase. It was established in [3] that the temperature of complete transition of aluminium hydroxide precursor into α-Al_2O_3 is lower for the higher concentration of seeding introduced and presumably for the higher uniformity of its distribution over the gel volume. As it follows from the data shown in Fig. 5, even 0.2 mass % of the seeding is sufficient for complete transition into the stable modification only at 930 °C.

One cannot exclude that in case of the non-uniform distribution of nanoparticles over the

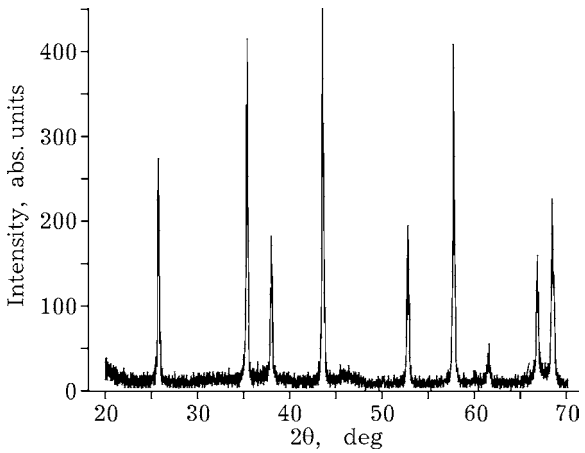

Fig. 4. X-ray diffraction patterns of sample No. 8 (see Table 1).

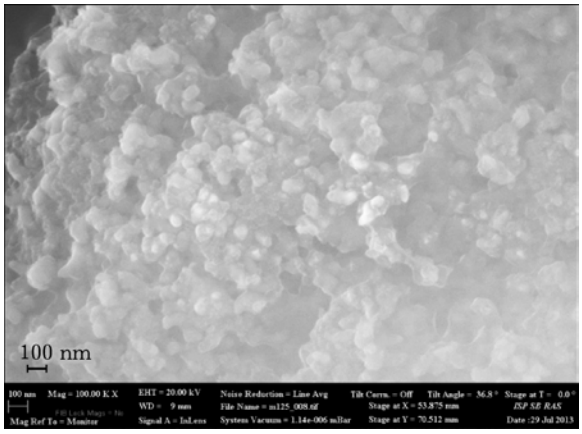

Fig. 6. Electron microscope image of gel annealed at 900 °C.

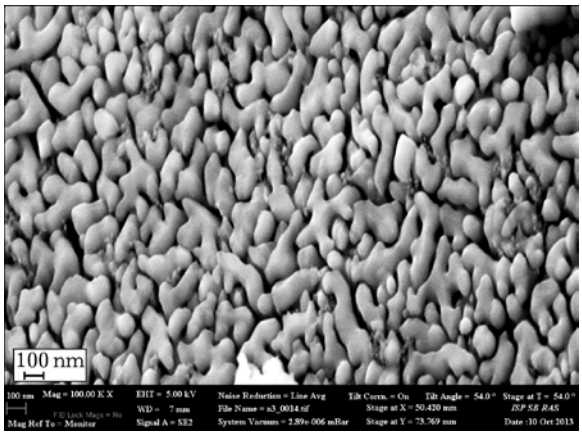

Fig. 7. Electron microscope image of gel sample annealed with the particles adhered to each other.

aluminohydroxide precursor there are regions, in which the transition proceeds much earlier than in the neighbouring regions which are depleted of seeding particles. As a result, the particles of freshly formed α-modification will be surrounded by the amorphous or metastable phase (Fig. 6). According to the data presented in Fig. 7, crystallization of these regions partially proceeds at 930 °C even without seeding, which results in adhesion of their neighbouring particles to each other, so worm-like formations appear.

It is very difficult to control the uniformity of seeding particle distribution, especially keeping in mind their tendency to get aggregated. At the same time, it is known that the tendency to coagulation exhibited by the suspension containing seeding nanoparticles depends on the amount of ions (especially multiply charged) present in it. The X-ray diffraction patterns of annealed gels recorded under identical conditions in parallel experiments but with water of different purification degrees as a solvent are shown in Fig. 8.

The degree of the transition into α-modification in the case of deionised water turned out to be noticeably higher. The sequence of transformation amorphous gel > metastable oxide > α-Al_2O_3 is clearly distorted. The change of X-ray diffraction patterns of the gel obtained in deionised water under heating with the rate of 12 °C/min, followed by the exposure at the temperature for only 10 min and heating to the next temperature is shown in Fig. 9.

Even at 500 °C we observe a clear formation of α-modification, while metastable phases appear only at 700 °C and afterwards disappear at temperatures above 900 °C. In the case of gel exposure for 1 h at 500 °C the X-ray diffraction pattern corresponds to a mixture of amorphous phase and α-phase 45–50 nm in size at the approximate ratio of 1 : 4 and does not contain reflections attributed to intermediate modifications.

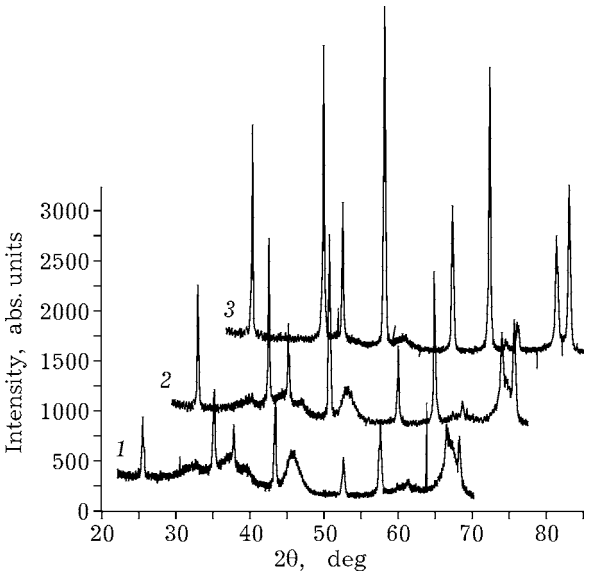

Fig. 8. X-ray diffraction patterns of gels annealed at 930 °C with 3 mass % seeding, prepared in technical grade (*1*), distilled (*2*) and deionised (*3*) water.

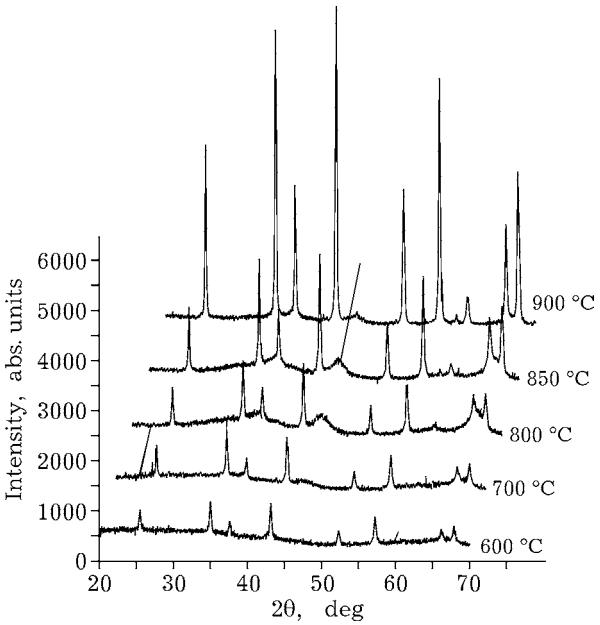

Fig. 9. X-ray diffraction patterns *in situ* of gel annealed with 3 mass % seeding at different temperatures.

So, gel structure formed in the vicinity of seeding particle seems to be favourable for the formation of α-Al_2O_3 nuclei in it without high activation barriers. It should be noted that natural aluminium hydroxide diaspore, due to its structure, is transformed at approximately the same temperature directly into α-modification omitting intermediate phases [6]. Crystallization in lean regions proceeds in a usual manner through the formation of metastable oxide phases. Finally, the smaller is the number of these regions, the lower is the temperature of 100 % transition, so the lower is the amount of possibilities for particle coalescence. Therefore, it is necessary to achieve maximally uniform distribution of seeding particles over the gel, which will provide the minimal temperature of α-Al_2O_3 crystallization and maximally favourable properties of α-Al_2O_3 nanopowders with respect to ceramic production (moldability, aggregating ability, and sintering ability).

CONCLUSION

After the introduction of α-Al_2O_3 nanoparticles in the amount of 0.2–5 mass % into the gel formed by hydrolysis of aluminium nitrate, crystallization of the thermodynamically stable modification accelerates; as a consequence, the temperature of 100 % transition within definite time decreases. The higher is seeding concentration, the lower is the temperature, at which it is possible to obtain monophase α-Al_2O_3. Under conditions of temperatures within 800–900 °C, the product consists of nanoparticles of 45–60 nm in size. At the same time, powders of the same size demonstrate a different sintering ability at 1300 °C. This is likely due to the nonuniform distribution of seeding over the volume of gel, as a result of which, in some cases particles splice with each other.

When deionised water is used instead of distilled water, α-modification is formed even at 500 °C, moreover, directly from the amorphous gel bypassing intermediate phases.

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