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Obtaining Nanocrystalline α -Al₂O₃ by Introducing a Seeding Agent into Precursors

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Abstract

By introducing α -Al₂O₃ powder with particle size 25 nm, in the amount of 1–10 mass %, into the solution of aluminium nitrate or into dry aluminium hydroxide, the kinetics of the formation of the stable α -phase during subsequent heating of the precursor gets accelerated substantially. Depending on the amount and method of introducing the seeding agent, the complete transformation of the precursor into α -Al₂O₃ occurs at a temperature within the range 800 to 930 °C. The powder formed at such a low temperature is composed of porous aggregates 10–20 mm in size; the size of crystallites comprising the aggregates is independent of the amount of seeding agent introduced and is equal to approximately 50–60 nm. Grinding under soft conditions leads to the destruction of aggregates and to the formation of nanopowder which is active towards caking. Later on, a ceramic material with the porosity at a level of 1 % is obtained from the powder at 1450 °C.

Key words: α-aluminium oxide, nanopowder, synthesis, caking

INTRODUCTION

To obtain ceramic powder of high-purity aluminium oxide, precipitation of pure aluminium salts (chloride, nitrate, sulphate) is used, followed by thermal treatment of the formed oxide. The latter process is accompanied by its transformation into oxyhydroxides and then into various transition forms of oxide, the last one of which is thermodynamically stable α -modification. For example, boehmite (γ -AlOOH) > γ > $\delta > \theta > \alpha$ -Al₂O₃ [1]. It is α -modification that is mainly used in ceramic production because phase transitions of transient forms that proceed together with sintering destroy the material.

All the transformations of different forms of aluminium oxide are well studied [2–4]. It was established that until θ -Al₂O₃ the transitions are topotactic, that is, without cardinal changes of the crystal structure of boehmite. These transitions are accompanied only by the

removal of water molecules and, as a consequence, the formation of porosity, as well as subsequent transformation of pores due to aluminium oxide compacting. The transformation into the stable α -modification is linked with a substantial rearrangement of the structure and requires overcoming a high activation barrier which is necessary for the formation of nuclei of the new phase. Because the stage of nuclei formation limits the rate of phase transition, the product is composed of a "small" number of coarse particles that are tightly cohered to each other to form agglomerates at the high transition temperature.

Many researchers tried to reduce the temperature of α -Al₂O₃ formation by introducing the particles of various oxides as a seeding (up to 5 mass %) thus artificially introducing crystallization centres. For this purpose, the oxides of copper, iron, chromium, magnesium were tested. It was demonstrated that in a number

of cases the temperature of $\alpha\text{-}Al_2O_3$ formation can be reduced from ~1200 to 1050 °C. In 1985, through multiple sedimentation of a dispersion of commercial aluminium oxide powder (A-16SG, Alcoa Inc.), the fraction with the average size of 0.1 mm was isolated [5]. This allowed one to study the effect of seeding of that powder on the formation of α -Al₂O₃ from commercial boehmite (Catapal SB, Vista Chemical). For this purpose, aluminium oxide with particle size of 0.1 µm was added into a transparent sol of boehmite, the sol was heated with an electric range until the gel was formed. It was shown that the temperature of complete crystallization of α -Al₂O₃ decreases with an increase in the concentration of the seeding, achieving 1025 °C for 10 % (per the dry mass). In this situation, the grain size does not exceed $0.1-0.4 \,\mu m$ because low temperature prevents the growth of α -Al₂O₃ particles and thus promotes the formation of finer dispersed powder. An attempt for further reduction of the temperature of α -phase crystallization due to the use of a seeding with the size of α -Al₂O₃ particles about 25 nm [6] showed that a 100 % transition may be achieved even at 900 °C with the grain size of the product at a level of 45–50 nm.

During the recent years, attention to obtaining aluminium oxide nanopowders through commercially efficient method has increased. The goal of this work was to provide systematic investigation of the effect of seeding of α -Al₂O₃ nanopowder on the properties of the aluminium hydroxide gel product obtained through crystallization.

MATERIALS AND METHODS

The reagents used in the work were Al(NO₃)₃ \cdot H₂O and aluminium hydroxide (GOST 11841– 66, X-ray diffraction patterns correspond to gibbsite) of ch.d.a. reagent grade, 25 % ammonia solution of kh.ch. grade. Nanopowder α -Al₂O₃ with average particle size about 25 nm obtained according to the procedure described in [7] was used as a seeding. The concentration of iron admixture in the nanopowder was 0.15 %.

The X-ray phase analysis of powders and sintered materials was carried out on a DRON-4 X-ray diffractometer ($CuK_{\alpha 1}$ radiation, graph-

ite monochromator). Determination of the size of crystallites in powders was carried out with the help of PowderCell 2.4 software taking into account the instrumental line broadening determined during recording the reflections from corundum plates annealed at 1800 °C. High-quality description of the X-ray peaks of the formed intermediate phases of aluminium oxide was hindered, so the data for γ -Al₂O₃ were always included into the program as the second phase for the quantitative phase analysis. Because of this, the data on the content of α -Al₂O₃ in the product should be considered only as a rough approximation.

The specific surface of powders was determined with the help of Sorbtometr set-up by means of the thermal desorption of nitrogen. Examination of the granulometric composition was performed with a Nicomp 380 ZLS laser granulometer (USA). Electron microscopic analysis was carried out using a JEM 2000 FX2 transmission electron microscope (Japan).

Powder grinding was performed using AGO-2M planetary mill (with the cylinder and balls made of wear-resistant ceramics based on ZrO₂).

Thermal treatment of the samples was carried out with a VP 04/17 furnace (Russia) in the air with temperature control accuracy of ± 1 °C.

RESULTS AND DISCUSSION

Ultrasound-frothed aqueous (pH 3.5) suspension of α -Al₂O₃ nanopowder was poured into the aqueous solution of aluminium nitrate under intense mixing. During vigorous agitation, 25 % ammonia solution was added drop by drop into the suspension heated to 70 °C; the amount of added ammonia solution was calculated according to equation

 $Al(NO_3)_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4NO_3$

The resulting gel was aged for about 12 h, dried on electric range and then heated in the furnace at a rate of $5 \,^{\circ}$ C/min to different temperature points, followed by subsequent isothermal exposure. The X-ray phase analysis was carried out.

The diffraction patterns of gel samples heated under identical conditions, containing the seeding or not, are presented in Fig. 1. One can see that the gel containing no nanopowder



Fig. 1. X-ray diffraction patterns of gel samples heated for 30 min at 930 °C. Seeding concentration, mass %: 1.5 (a), 0 (b).

is transformed into the transient forms of aluminium oxide, while the gel with seeding is a well crystallized α -Al₂O₃ phase with crystallite size 55 nm and specific surface S = 32-34 m²/g. Particle size (*D*), determined using equation *D* = 1.5/*S*, was 44-47 nm.

It follows from the data shown in Fig. 2 that the only crystalline phase in the powder heated at 200 °C is ammonium nitrate; amorphous product remains after its decomposition. Subsequent short-term heating at 870 °C leads to the appearance of mainly transient forms of aluminium oxide in the diffraction patterns but after 910 °C α -Al₂O₃ becomes the major phase, though the transition into thermodynamically stable modification is incomplete yet under these conditions. This is confirmed also by the specific surface of powder, which exceeds 150 m²/g. This in no way corresponds to the profile of the X-ray peaks of α -phase. Residues of other aluminium oxide forms are likely to be conserved



Fig. 2. X-ray diffraction patterns of the gel containing 1.5 mass % of seeding (per dry product): a, b – heated for 1 h at 200 and 340 °C, respectively; c, d – heated for 20 min at 870 and 910 °C, respectively.

in the powder, which determines the high specific surface of the powder.

It follows from the data shown in Table 1 that the size of crystallites of the formed oxide is almost independent of the concentration of seeding introduced into the gel. It should be stressed that a 100 % transition into the α -phase at 910 °C and seeding concentration of 1.5 mass % does not contradict the data shown in Fig. 2 because preliminary heating of this sample at 870 °C has already brought about a definite contribution into the final result.

On the basis of the fact that the size of crystallites does not depend on the amount of seeding, we conclude that the particles of the introduced seeding do not play the part of the nuclei of the new phase. Otherwise the final size of the formed α -Al₂O₃ crystallites would decrease with an increase in the number of nuclei.

In addition, in the case of the concentration of the seeding is 1.5 mass %, the volume of

TABLE 1

Effect of seeding concentration (per dry product) on crystallization and grain size of α -Al₂O₃ (time of isothermal exposure: 20 min)

| Seeding | Content of α -phase, % Temperature, °C | | Size of α -phase crystallites | |
|----------------|--|-----|--------------------------------------|---|
| concentration, | | | after heating at 910 °C, nm | |
| mass % | 870 | 910 | | |
| 1 | 13 | 68 | 62 | |
| 1.5 | 40 | 100 | 61 | |
| 3 | 40 | 100 | 69 | |
| 8 | 42 | 100 | 58 | |
| 10 | 40 | 100 | 55 | _ |

the growing nuclei should increase by a factor more than 65 in order to fill the entire volume of the material with the growing nuclei, and this corresponds to a more than 4-fold increase in the size of nuclei. So, if only artificially introduced seeding particles are growing, the final size of the crystallites of α -phase cannot be less than 100 nm, though this contradicts the experimental results. The authors of [5] established the following fact: in spite of the 100 nm size of the introduced seeding, the size of the majority of grains of α -Al₂O₃ phase formed at 1025 °C, at the 95 % transformation degree, was about 50 nm and only afterwards increased to 0.1–0.4 µm.

As an alternative version of the explanation of seeding effect, we may assume that its particles affect the structure of aluminium hydroxide gel formed around them, or they affect the structure of the forming transient oxide forms decreasing the activation energy for the transition into α -Al₂O₃. In this case, it appears logical that a decrease in the activation energy of the transformation will be larger for a larger number (but not concentration) of seeding particles. In other words, the smaller is the number of seeding particles, the larger is the distance between them, and the lower is the probability for the formation of α -Al₂O₃ nuclei in the regions that are remote from those particles. Thereby, at a given temperature, longer time will be needed for complete transformation, or at a given time of experiment higher temperature will be needed.

As far as the size of α -Al₂O₃ crystallites in the product is concerned, it must be stressed that the density of α -modification is much higher than the density of the gel or transient forms of aluminium oxide. Therefore, elastic strain should inevitably arise in the matrix of the transient oxide during the formation of a nucleus. That strain cannot relax under the conditions of the absence of sufficient diffusion mobility of lattice elements at low temperature. With nucleus growth, the strain increases and at a definite nucleus size the strain exceeds some critical threshold after which the particle of the new phase most probably gets detached from the matrix, and its growth stops. It is this reason for which the size of α -Al₂O₃ particles is independent of the amount of introduced

seeding; the data obtained by us (Table 1) almost coincide with the results reported in [5]. At 1025 °C, the diffusion mass transfer was likely to provide further growth of the grains detached from the matrix from 50 to 100-400 nm, while at 920 °C the diffusion mass transfer appears to be insufficient.

In the case if the above considerations are true, at a temperature below 1000 °C a decrease in the number of seeding particles (provided that their mass is constant) should not have a substantial effect on the size of α -Al₂O₃ particles, but should lead to a decrease in the temperature of 100 % crystallization of the oxide within a definite time interval.

To verify this hypothesis, we centrifuged the aqueous suspension containing the seeding particles, for 10 min at the acceleration of 2000g. Thus isolated finest fraction (10 %) was introduced into the solution of aluminium nitrate in the amount providing 2 mass % of seeding calculated per final α -Al₂O₃. Crystallite size in the fine fraction turned out to be even insignificantly larger in comparison with that for initial seeding (~28 nm), which is due either to the low accuracy of size determination or to predominant aggregation of the smallest particles.

After exposure at 900 °C for 30 min, 100 % α -Al₂O₃ is identified in the diffraction patterns. Crystallite size turned out to be approximately the same (52 nm), and specific surface was 32 m²/g. So, due to a decrease in seeding particle size, we succeeded in reducing the temperature of the complete transformation by 30 °C more; the size of crystallites in the product remained approximately the same (50–60 nm).

The product looks like a pale yellow material composed of porous granules 1-2 mm in size. Grinding with light ceramic balls in ethanol at the acceleration of 4-6g for several minutes causes the destruction of granules but does not affect specific surface. The colour of powder becomes grayish; according to the data of optical microscopy, it is composed of the particles about 20 µm in diameter; as a result of attrition in liquid, their size decreases to less than 1 µm. If we place a small amount of the powder in weakly acidic aqueous medium and subject it to short-term ultrasonic action, particles with a size of 50 nm are formed after the destruction of the granules (Fig. 3). The



Fig. 3. Numerical (1) and volume (2) particle size distribution in the powder obtained at 900 °C and ground for 5 min with the acceleration of 4g.

average size determined from the volume distribution is equal to 300 nm, which points either to the fact that 5 min is insufficient grinding time for the complete destruction of all the agglomerates, or to the formation of agglomerates of particles directly in the suspension.

The data of the electron microscopic studies of dried suspension are shown in Fig. 4. These data provide unambiguous evidence that the size of powder particles is about 50 nm. So, the product of low-temperature crystallization is indeed composed of crystals loosely packed into granules 50 nm in size, and weak mechanical action can easily destroy the granules to form individual crystallites.

It is important to understand that the size of crystallites comprising the seeding (in our case 25 nm) cannot determine the seeding efficiency. Finally, the uniformity of crystallite distribution over the precursor of α -phase is important. It is known that dry nanopowder is composed of aggregates; their strength depends on the method of their preparation. In our case, there are no data providing evidence of the complete destruction of aggregates during the formation of seeding suspension, so we cannot exclude that seeding particles are distribution over the material non-uniformly. The above-described centrifuging procedure might have removed only the largest aggregates.

A more efficient method to destroy aggregates excluding re-aggregation can be the joint grinding of nanopowder with a definite amount of aluminium nitrate. The suspension introduced into the solution was formed from thus prepared weighted portion; no change of seeding crystallite size after grinding with the salt for 10 min at the acceleration of 15g occurred. It turned out that the use of this procedure in the case if the concentration of the seeding is 5 mass % allows us to achieve a complete transformation into α -modification of aluminium oxide for 30 min at a temperature as low as 850 °C. The specific surface of thus obtained product is $32 \text{ m}^2/\text{g}$, crystallite size is 60 nm. It is interesting that further heating for 30 min at 900 °C does not cause any change of crystallite size, that is, mass transfer under these conditions is indeed unable to provide noticeable growth of the crystallites.



Fig. 4. Aqueous suspension of the powder obtained at 900 °C, and ground for 5 min with the acceleration of 4g in ethanol.



Fig. 5. SEM image of powder obtained at 950 °C and ground for 5 min with the acceleration of 4g in acetone.



Fig. 6. Structure of aggregate obtained at 950 °C and ground for 5 min with the acceleration of 4g in acetone.

One can see in the data presented in Fig. 5 that after grinding at 4-6g for 5 min in acetone, the powder dried in the air is composed of porous aggregates $10-20 \ \mu m$ in size, in turn, composed of equal-sized spherical particles about 60 nm in diameter (Fig. 6).

If the concentration of the seeding is decreased to 3 mass %, the X-ray diffraction patterns of the powder heated at 850 °C reveals the peaks corresponding to α -Al₂O₃ with crystallite size 53 nm and small broad peaks of the transient forms of aluminium oxide. The high specific surface (60 m²/g) also points to the incomplete phase transition. Subsequent heating for 30 min at 900 °C allows us to complete the formation of α -Al₂O₃; crystallite size remains the same, to an accuracy of 5 %.

It is interesting that this powder is easily moulded by dry pressing and after annealing in the air at 1450 °C achieves the density of 3.94-3.95 g/cm³, which is 99 % of theoretically possible one. So, the residual porosity does not exceed 1 %.

Evidently, the addition of seeding through poring the suspension into the solution of aluminium nitrate does not allow us to achieve complete absence of aggregated particles in the precursor. Agglomerates can and must be formed after the addition of event he ideally prepared suspension of seeding nanoparticles into nitrate solution: the authors of [8] thoroughly studied the effect of multicharged cations present in solution on the changes in the parameters of the double electric layer and coagulation of the suspension. It appeared interesting to verify the universal character of above conclusions under other conditions of precursor formation and to eliminate the mobility of seeding particles which makes them agglomerate in nitrate solution.

For this purpose, a mixture of aluminium hydroxide and α -Al₂O₃ nanopowder (5 mass %) was activated in the mill under the acceleration of 10-25g for 20 min. Then the resulting dry powder was heated in the furnace at different temperatures. It turned out that monophase α -Al₂O₃ (Fig. 7, *a*) is already formed after treatment with the acceleration of 15g



Fig. 7. X-ray diffraction patterns of the mixtures of aluminium hydroxide with nanopowder in the concentration of 5 (*a*) and 1 % (*b*, *c*) activated for 20 min at 15*g* and heated at 800 (*a*, *b*) and 850 °C (*c*).

and more, after heating for more than 20 min at 800 °C; crystallite size is about 50 nm. If we decrease the acceleration to 10g, or decrease the concentration of the seeding at 15g to 1 mass %, higher temperature will be necessary for 100 % transition into the α -phase (see Fig. 7, b, c); however, this has almost no effect on crystallite size in the product.

It is interesting to stress that no comparable effects under similar conditions are observed for activation of aluminium hydroxide in the mill without seeding or for the replacement of planetary mill by a mortar or a roller mill (treatment time 6 h).

CONCLUSIONS

After the introduction of α -Al₂O₃ nanopowder (1–10 mass %) with particle size 25 nm as seeding into the solution of aluminium nitrate or into dry aluminium hydroxide, the formation of the stable α -phase after subsequent heating of the mixture requires much lower temperature. The maximal effect is achieved in the case of the maximal number of seeding nano-

crystallites uniformly distributed in the precursor, which allows us to obtain a monophase product even at 800 °C. The size of the crystallites of aluminium oxide formed at 800–930 °C is independent of the amount of seeding and is equal to approximately 50–60 nm. Grinding under soft conditions of α -Al₂O₃ obtained at low temperatures leads to the formation of the powder active with respect to sintering; ceramic material with the porosity about 1 % is obtained from the powder at 1450 °C.

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