Effect of the synthesis temperature on the phase composition of Al2O3

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Abstract. This work is devoted to studying the effect of the synthesis temperature on the phase composition of Al2O3. Aluminum hydroxide was obtained by a reverse heterophase deposition method. This method makes it possible to obtain the purest hydroxide powder. For the synthesis, several different temperature regimes were selected in the temperature range from 250°C to 1100°C.

1. Introduction

Today more and more companies are working towards the development of nanotechnology, as the most promising technology in such areas as nanobiotechnology, pharmaceuticals and medicine, nanoelectronics and the creation of new materials [1]. Nano dispersed metal oxides are used in the chemical industry [2], medicine, cosmetics, radio electronics, agriculture, they are also used to create new functional materials with special magnetic, electrical, optical properties, or when modifying polymer materials as fillers for polymers to improve the main indicators, such as mechanical, physical-chemical, chemical, etc. [3]. The properties of nanosized particles of metal oxides are due both by the features of individual particles and by the conglomerates formed by these particles [3]. The nano-sized structure of ceramics provides a denser packing and an increase in the mechanical properties of ceramics [4].

Materials based on aluminum oxide are widely used in those areas where high wear resistance, hardness, bending strength, and corrosion resistance of products are required. [4] Aluminum oxide is used in oil refining and petrochemistry [5], in the modern industry to obtain composite ceramic materials with improved characteristics [6], as the most promising filler for composite materials for aviation and space technology [7].

The structure and dispersion of nanomaterials depend on the method of their preparation [3]. Currently, there are many methods for obtaining ultradispersed materials: gas-phase synthesis, the use of low-temperature plasma, cathode sputtering, mechanical and ultrasonic dispersion, synthesis of particles in reduction reactions, cryochemical method, thermal decomposition, electrochemical method, sol-gel method [8]. All these methods can also be divided into two large groups: based on the dispersion (grinding) of the starting materials, the so-called "top-down" method, and methods based on condensation from atomic and molecular formations - the "bottom-up" method [8]. The methods belonging to the first group have one significant drawback: the chemical purity and phase composition of the ultrafine powder depends on the starting material. Methods using chemical reactions are
preferable since they allow you to control the shape and size of particles, phase, and impurity compositions [9].

It is known that oxides having the same composition and the same particle shape, but obtained by different methods, can differ significantly physical and physicochemical properties. [3]. Aluminum oxide is obtained mainly by the method of heat treatment of various modifications of aluminum hydroxides [2], which, in turn, can be obtained by various methods of chemical [10] and electrochemical deposition. The properties of aluminum oxides (phase composition, specific surface area, pore-volume, and their size distribution, physicochemical properties) depend on the properties of hydroxides from which they were obtained, under the action of the mechanism of phase transitions in the alumo-oxygen system [2,11]. By changing the methods of obtaining aluminum oxide, as well as the conditions of its heat treatment, it is possible to obtain a powder with different properties [11].

In this work, a chemical method was used, which makes it possible to obtain the more purely oxide powder, consisting of two stages:

1. Obtaining aluminum hydroxide by the method of reverse heterophase deposition of a saturated solution of aluminum nitrate into an aqueous solution of ammonia.
2. Synthesis of aluminum oxide powder from aluminum hydroxide at different temperature conditions.

At the first stage, it is possible to regulate the purity of the final product using by starting reagents of various purities and concentrations. At the second stage, it is possible to regulate the phase composition and dispersion of the powder by changing the synthesis temperature.

This work is devoted to studying the effect of the synthesis temperature on the phase composition of Al2O3 obtained using the method of reverse heterophase deposition.

2. Source materials and equipment

For the synthesis of aluminum oxide, pure aluminum nitrate powder for analysis (VWR CHEMICAL) was used as a starting material, which was dissolved in distilled water in proportions of 1:3. The resulting solution was boiled at a temperature of 116°C and brought to a saturated state. A saturated salt solution was sprayed under air pressure through a spray funnel into a precipitator, which was used as an extra pure aqueous ammonia 23-5 ("Component-Reagent"). The excess ammonia with respect to the salt solution was 10 to 1. The air supply pressure during spraying was 2 atmospheres.

As a result of spraying a saturated salt solution into the precipitator, aluminum hydroxide precipitated, which was washed with distilled water to pH=8. The final washing was carried out with ethyl alcohol of 95% purity. After that, the powder was dried at room temperature until it was completely dry.

The synthesis of aluminum oxide from aluminum hydroxide powder was carried out in a furnace with disilicide-molybdenum heaters in corundum crucibles. In this work, several different temperature regimes were selected in the temperature range from 250-1100°C. The isothermal holding time at the maximum temperature was 2 hours.

The synthesis of aluminum oxide was carried out in a furnace with disilicide-molybdenum heaters Nabertherm. To identify the phase and chemical composition was used, X-ray diffraction analysis was used (XRD DRON-3 diffractometer, CuKα radiation, λ = 1.5406 Å, scanning speed 2θ = 2 deg/min). The phase composition was identified using COD database [12, 13]. Morphology and the samples' structural features were studied by scanning electron microscopy (SEM) (electron microscope Tescan Vega II SBU).

The quantitative ratio of the phases was calculated using the Rietveld method [14].

3. Results and discussion

Figures 1 and 2 show the results of the X-ray phase analysis of the powder after heat treatment.

X-ray phase analysis of the powder, after heat treatment at 250°C for 2 hours (figure 1(a)), shows that the powder is aluminum hydroxide, namely boehmite (a mineral from the class of hydroxides with the chemical formula γ-AlO(OH) (96-901-2276)) with an orthorhombic crystal lattice. The
diffractogram of the powder, after heat treatment at 300°C for 2 hours (figure 1(b)), shows that the powder is also boehmite $\gamma$-AlO(OH) (96-901-2276) with an orthorhombic crystal lattice.

After heat treatment at 400°C for 2 hours, X-ray phase analysis shows that an amorphous halo is observed, this indicates an incomplete crystallization of the aluminum oxide. In this case, the phase composition is represented by two polytypes $\gamma$-Al$_2$O$_3$ (96-101-0462) and $\eta$-Al$_2$O$_3$ (96-120-0016), differing from each other in the parameters of the cubic crystal lattice. For $\gamma$-Al$_2$O$_3$ - $a=3,95$ (6,1% of the mass), and for $\eta$-Al$_2$O$_3$ - $a=7,906$ (93,9%).

![Diffractogram patterns of aluminum oxide powders after heat treatment at temperatures 250°C (a), 300°C (b) and 400°C (c).](image-url)

**Figure 1.** Diffractogram patterns of aluminum oxide powders after heat treatment at temperatures 250°C (a), 300°C (b) and 400°C (c).
Figure 2. Diffractogram patterns of aluminum oxide powders after heat treatment at temperatures 500°C (a), 700°C (b), 900°C (c) and 1100°C (d).

X-ray phase analysis of the powder synthesized at 500°C for 2 hours (figure 2(a)), also shows the presence of two polytypes $\gamma$-$\text{Al}_2\text{O}_3$ (5.1%) and $\eta$-$\text{Al}_2\text{O}_3$ (94.9%).

With an increase in the synthesis temperature to 700°C (figure 2(b)), it can be seen that, with the same phase composition, the amount of the $\gamma$-$\text{Al}_2\text{O}_3$ phase with a cubic crystal lattice with parameters $a=3.95$ decreases to 1.7%, and the mass fraction of the second phase $\eta$-$\text{Al}_2\text{O}_3$ with a cubic crystal lattice with parameters $a=7.906$ is 98.3%.

The phase composition of aluminum oxide powder after heat treatment at 900°C (figure 2(c)), consists of two phases of cubic $\eta$-$\text{Al}_2\text{O}_3$ with parameters $a=7.906$ and monoclinic $\theta$-$\text{Al}_2\text{O}_3$ (96-120-0006). The mass fraction of $\eta$-$\text{Al}_2\text{O}_3$ is 81.9%, and $\theta$-$\text{Al}_2\text{O}_3$ is 18.1%. The $\gamma$-$\text{Al}_2\text{O}_3$ phase is absent.

According to the results of X-ray phase analysis of the powder heat-treated at a temperature of 1100°C (figure 2(d)), the main phase is $\alpha$-$\text{Al}_2\text{O}_3$ – corundum (96-230-0449) and its fraction is 97.9%, the fraction of phase $\theta$-$\text{Al}_2\text{O}_3$ is 2.1%.

Figure 3 shows micrographs of aluminum oxide powders synthesized at 500°C and 700°C. There are spherical particles with a diameter of 70-80 μm, which are obtained during the deposition of aluminum hydroxide. With an increase in the synthesis temperature, their number decreases, since they are destroyed during the crystallization of the aluminum oxide.
Figure 3. Micrograph of alumina powders synthesized by 500°C (a) and 700°C (b).

The summary data on the quantitative ratio of the phases depending on the synthesis temperature in the range 250-1100°C are given in the table 1.

Table 1. Dependence of the phase composition of the Al2O3 powder on the synthesis temperature.

| Heat treatment temperature, °C | Phases present                        | Crystal system | Cell parameters | Phase content, wt.% | Reference code |
|--------------------------------|---------------------------------------|----------------|-----------------|----------------------|----------------|
| 250                            | γ-AlO(OH) (Bohmite)                    | Orthorhombic   | a=2.867, b=12.219, c=3.692 | 100                  | 96-901-2276    |
| 300                            | γ-AlO(OH) (Bohmite)                    | Orthorhombic   | a=2.867, b=12.219, c=3.692 | 100                  | 96-901-2276    |
| 400                            | γ-Al2O3 (Aluminium oxide – gamma)      | Cubic          | a=3.95          | 6,1                  | 96-101-0462    |
|                                | η-Al2O3 (Aluminium oxide – eta)        | Cubic          | a=7.906         | 93,9                 | 96-120-0016    |
| 500                            | γ-Al2O3 (Aluminium oxide – gamma)      | Cubic          | a=3.95          | 5,1                  | 96-101-0462    |
|                                | η-Al2O3 (Aluminium oxide – eta)        | Cubic          | a=7.906         | 94,9                 | 96-120-0016    |
| 700                            | γ-Al2O3 (Aluminium oxide – gamma)      | Cubic          | a=3.95          | 1,7                  | 96-101-0462    |
|                                | η-Al2O3 (Aluminium oxide – eta)        | Cubic          | a=7.906         | 98,3                 | 96-120-0016    |
| 900                            | η-Al2O3 (Aluminium oxide – eta)        | Cubic          | a=7.906         | 81,9                 | 96-120-0016    |
4. Conclusion:
As a result of this work, the phase transitions of Al2O3 were studied depending on the temperature treatment of aluminum hydroxide obtained by the method of reverse heterophase deposition. At temperatures of 250°C and 300°C, the powder is AlO(OH) hydroxide with an orthogonal crystal lattice. At a synthesis temperature of 400°C, the Al2O3 oxide powder is represented by two polytypes γ-Al2O3 and η-Al2O3. With an increase in the synthesis temperature from 400°C to 500°C and from 500°C to 700°C, the mass fraction of γ-Al2O3 decreases. During thermal treatment of aluminum hydroxide powder at a temperature of 900°C, the θ-Al2O3 phase is formed, the amount of the η-Al2O3 phase decreases, and the γ-Al2O3 phase is absent. During heat treatment of aluminum hydroxide powder at a temperature of 1100°C, the powder is a phase of α-Al2O3 - corundum with an insignificant content of the impurity phase θ-Al2O3.

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