

An Effect of Relative Humidity on Hyperfine Grinding of α -Al₂O₃

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Abstract

An effect of conditions of hyperfine grinding on the size of crystallites and on the aggregation degree of received α -Al₂O₃ nanopowders has been examined. It has been demonstrated that the average size of crystallites of a mechanically grinded powder is a function of relative humidity in the barrels of a planetary mill with a pronounced minimum (200–250 Å) in the range of values of the relative humidity of 0.01–1 %. It has been found that the degree of the aggregation capacity of powders is also an extremal function of the relative humidity; however, its extremums are noticeable now at other values of the relative humidity. A decrease in the efficiency of grinding with practically complete (<0.01 %) absence of moisture in the atmosphere is possibly related to the facilitated recrystallization of particles in the aggregates that are tightly linked by electrostatic forces under conditions when there are no steric difficulties at the boundary between the crystallites.

INTRODUCTION

Hyperfine grinding of inorganic oxides, at first sight, is one of the most promising methods to obtain nanopowders thanks to the simplicity and inexpensiveness as it does not assume the use of special equipment, great volumes of liquids [1], and a higher than usual consumption of power resources [2]. Meanwhile, this method has not received a wide recognition in practice because of the emergence of serious restrictions as we pass to particles less than ~0.1 microns in size. These restrictions are determined by the highest activity of nanopowders, which leads to sticking and recrystallization of the particle constituents, as well as to their interaction with the medium, where their grinding takes place. Previously, we have analysed the basic, in our opinion, features of this process in a nanorange using hyperfine grinding of α -Al₂O₃ as an example [3]. It has been found that intensive mechanical treatment of inorganic oxides leads to the establishment of a dynamic equilibrium between the processes

that decrease the particle sizes (the grinding itself) and those of their aggregation with their subsequent recrystallization within an aggregate. The minimal average size of the produced nanoparticles is controlled by the position of this equilibrium that depends on specific conditions of the experiment and that can be controlled only by changing the conditions of the formation of the aggregates and recrystallization of the crystallites.

Further research in the direction of practical use of the found regularities and the ways to adjust the minimum achievable size of α -Al₂O₃ particles (150–500 Å) have demonstrated that while the qualitative character of the dependence of an average size of the produced nanopowder on the conditions of the mechanical treatment is preserved, a concrete value of the size that is attainable in identical conditions of the experiment may vary over a wide range. Results of the experiments that have been conducted during the winter and summer time period differ between each other to the maximum extent. In our opinion,

hypothetically significant factors that have an influence on the course of hyperfine grinding under Siberian conditions are the moisture content in the atmosphere of the laboratory and the temperature of tap water that cools the barrels. Moisture content in winter and summer periods varies from 1.5 to 15 mg/cm³; the temperature does from 7 to 25 °C, respectively. Apparent and sometimes critical influence of moisture and temperature of the cooling water on the mechanochemical reactions has been pointed out in the respective works [4] and [5]. This work is devoted to the investigation of the effect of these two factors on hyperfine grinding of α -Al₂O₃.

EXPERIMENTAL

Aluminium oxide of qualification "analytically pure" (ch.d.a.) (technical specifications 6-09-426-75) was calcined at 1170 °C in the air for 3 h, and then, according to XRD data, it represented 100 % α -Al₂O₃. Specific surface of the produced oxide comprised 6.7 m²/g. Hyperfine grinding of the powder was conducted in an AGO-2M planetary mill with the use of steel balls of diameter 10 mm and barrels. The ratio of the balls mass and a grinded oxide comprised 1 : 40, the developed gravitational acceleration was 40g, and time for mechanical treatment, 15 min. Water or a mixture of water and ethylene glycol that was forced by a pump with a constant flow rate was applied as a liquid for cooling the barrels. The temperature of the cooling fluid was maintained in a range of values from -30 to +120 °C by means of a thermostat by addition of ice or dry carbonic acid in case of need.

Before carrying out the experiments, the barrels with aluminium oxide were conditioned in exsiccators with water, silica gel, or calcium chloride at a certain temperature. The temperature in the exsiccators and the relative humidity were measured by a Rustermo hygrometer, and if low, the humidity was determined based on the reference data.

Before the determination of specific surface, the grinded powders were processed with 17 % solution of HCl within 1 h, and then they were several times washed with the same solution. A specific surface was measured by a Katakon

sorbometer based on thermal desorption of nitrogen. Based on five various p/p_0 values, a BET isotherm was plotted; the least square method was applied to calculate the BET constant and the quantity of the adsorbed nitrogen atoms per mass unit of the weighed sample.

X-ray diffraction analysis and determination of crystallite sizes were conducted in a DRON-4 diffractometer (CuK_a radiation with a graphite monochromator).

To determine the size of the crystallites, the use was made of a procedure to search for a true broadening of a diffraction line without any assumed kind of the function that describes the contour of the line [6]. Reflexes from <012> and <024> planes and reflexes from the reference aluminium oxide that has been annealed at 1600 °C were recorded at a speed of 0.05–0.2 deg/min. Based on the fact that the line from an experimental sample is a convolution of functions that describe an instrumental broadening (a line of the reference substance) and a broadening that is related to the characteristics of a grinded oxide, the mathematical operation of development was made. Subtraction of the K_{a2} component has been performed by means of the PowderX code.

The value of the integrated half-width b for a line of the true physical broadening that has been obtained in this way was determined as an area under the curve divided by the height of the peak in its maximum:

$$\beta = \int f(x)dx / I_{\max} \quad (1)$$

where I_{\max} is the height of the peak, $f(x)$ is the function of the physical broadening for the sample.

Taking into consideration the fact that the broadening of diffraction peaks that is related to particle sizes can be better described by the function $1/1 + ax^2$, and the broadening that is associated with distortions of the crystal lattice, in the form of $1/(1 + ax^2)^2$ [6, 7], the obtained values of the integrated half-widths were substituted into a set of equations that was developed in [6]:

$$\left\{ \begin{array}{l} \beta_1 = (m_1 + 2n_1)^2 / (m_1 + 4n_1) \\ \beta_2 = (m_2 + 2n_2)^2 / (m_2 + 4n_2) \\ m_2 / m_1 = \cos \theta_1 / \cos \theta_2 \\ n_2 / n_1 = \tan \theta_1 / \tan \theta_2 \end{array} \right. \quad (2)$$

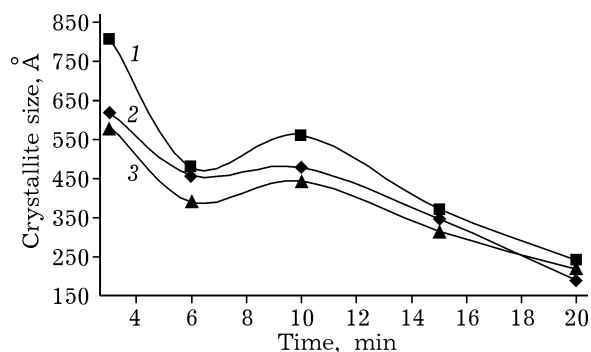


Fig. 1. Dependences of the size of crystallites on grinding time, recorded with the use of subtraction of the instrumental broadening following the Cauchy method (1), our method (2), and the Gauss method (3).

where n_1 , n_2 and m_1 , m_2 are the broadenings that have been caused by microdistortions and by fine dispersity respectively.

The size of the crystallites was calculated by the formula

$$D_{hkl} = 0.94 / (m_1 \cos \alpha_1) \quad (3)$$

Figure 1 displays the sizes of α - Al_2O_3 crystallites that were determined based on the given procedure as a function of the grinding time in certain arbitrary conditions of the experiment. It is evident that these values occupy an intermediate position between the points that were generated according to the traditionally accepted subtraction of a half-width of the reference substance (b_{ref}) from the integrated half-width of the sample (b_s) with the Cauchy ($b = b_s - b_{\text{ref}}$) or the Gauss method ($\beta = \beta_s^2 - \beta_{\text{ref}}^2$). Let us note that the discrepancy between the methods becomes very significant for large sizes of the crystallites (~ 800 Å).

This parameter that has been calculated with the formula $d = 6 / (\rho S)$, where ρ is the density of the material, S is the specific surface, is equal to 263 Å for a powder with the average size of the crystallites of ~ 250 Å that has been determined from the expression (3). On evidence of laser autocorrelation spectroscopy, 90 % of particles show an average size of 250 Å, which is also in good agreement with electron-microscopic data [8].

RESULTS AND DISCUSSION

Changes that occur in the diffractogram of α - Al_2O_3 as a result of its grinding are shown

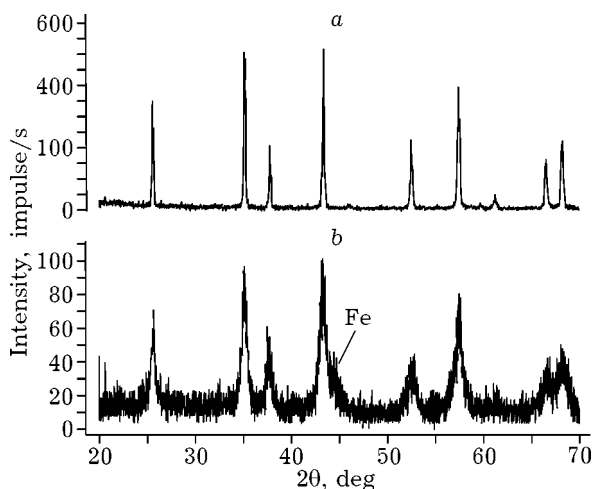


Fig. 2. Diffractogram of α - Al_2O_3 before (a) and after (b) grinding in an AGO-2 activator (40g, the grinding time is 15 min, 10-mm steel balls).

in Fig. 2. In addition to a significant broadening of peaks and to the emergence of an intensive reflex of α -Fe, no any changes are observed. Aluminium oxide remains in the form of α -modification. After treatment in HCl the reflex of iron dies out, and the size of the crystallites is practically unaffected. Meanwhile, about 15–20 mass % of the powder passes into solution. This means that part of oxide is amorphized, as it has been pointed out previously in [9], and it becomes soluble in an acid.

As opposed to the size, the specific surface of the crystallites increases several times after treatment in acid. This occurs as a result of the circumstance that the amorphized oxide and, possibly, metal iron stick the particles of crystalline oxide together within the aggregates. Removing the linking layer gives rise to a nanopowder of α - Al_2O_3 .

Shown in Fig. 3 is the dependence of the size of the crystallites of the α - Al_2O_3 nanopowder on the temperature of the liquid to cool the barrels and on the content of water vapour in the atmosphere of the barrel. It is evident that the dependence shows a rather complex nature with pronounced fields, where “coarse” and “fine” powders are realized. Consequently, it is impossible to recognize an interrelation between the size of the crystallites and the moisture content in the atmosphere without taking into account the temperature of the cooling fluid. Shown as an example in Fig. 4 is the result of our initial research of

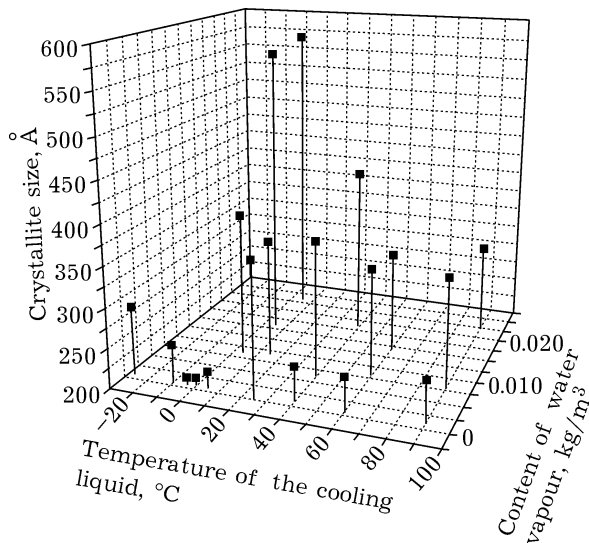


Fig. 3. Crystallite size *versus* the cooling temperature and the content of water vapour.

the reasons that would explain irreproducibility of the results.

We have demonstrated previously in [3] that consolidation of fine particles into aggregates with the subsequent transformation of the microstructure of the aggregate occurs in parallel with destruction processes during intensive mechanical treatment of nanopowders. Both of processes must be controlled to a large measure by the nature of adhesion between particles. With an increased adhesion, the friction coefficient between the particles grows (which facilitates more efficient grinding), and so does the tendency of the particles to be aggregated.

Based on the results of the examination of numerous data, the work [10] makes a conclusion that the relative humidity and not

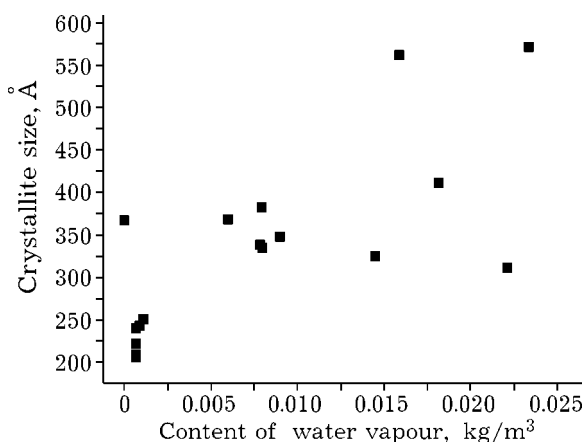


Fig. 4. Crystallite size *versus* the content of water vapour.

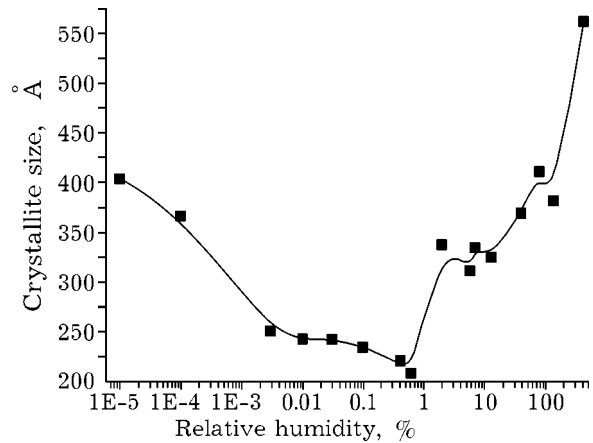


Fig. 5. Crystallite size *versus* the relative humidity in the activator.

the moisture content in the surrounding atmosphere has an effect on the adhesion between particles. The relative humidity encloses information not only about the water vapour available in the atmosphere, but also about the temperature, *i.e.* about the degree of molecular adsorption on the surface.

In this relation, we have tried to present the data in the Fig. 3 as a two-dimensional dependence of the size of the crystallites on the relative humidity of the atmosphere in the barrel (Fig. 5). Since it is impossible to measure this parameter during the experiment, it was calculated based on the data on the amount of moisture in the atmosphere of the barrel before grinding and on the temperature of the cooled wall of the barrel. It is believed that the temperature of an internal wall of the barrel differs slightly from the temperature of the liquid-cooled external wall and that it is the processes of condensation and evaporation on the surface of the internal wall that control the magnitude of the relative humidity.

Certainly, this is a rough assumption, because an aluminium oxide surface that is free from adsorbed atoms is formed during grinding and the surface sorbs moisture by the mechanism of chemical, instead of physical adsorption. Consequently, the relative humidity may be actually less than that we have calculated. Nevertheless, in our opinion, the extremal dependence that is depicted in Fig. 5 will be qualitatively unaffected. The point that matches the moisture content that is more than 100 % is shown arbitrarily and it means that the quan-

tity of water in the barrel exceeds the quantity that is required to reach the saturated vapour pressure at the given temperature.

Thus the size of crystallites of α - Al_2O_3 nanopowder that is formed because of hyperfine grinding depends essentially on the relative humidity during the mechanical treatment and it shows a pronounced minimum. The last-mentioned can be related to an increase of adhesion between particles due to the emergence of capillary attraction forces during the formation of layers or clusters of planar water on their "dry" surface. In parallel with this, the friction coefficient and consequently the grinding efficiency will increase in this case and will reach its maximum. However, according to [10], an adhesion maximum that is caused by capillary effect is observed in the field of values of relative humidity of 30–50 %. Let us note that a study of tribological properties of a film from tetragonal nanocrystalline ZrO_2 [11] has also shown a sharp maximum of the friction coefficient that is available approximately at the 40 % relative humidity. Consequently, the found minimum (see Fig. 5) most likely is of some other nature.

In our opinion, there can be two reasons for the increase of the average size of crystallites in the field of minimal values of the relative humidity. In the first place, this may occur owing to a substantial growth of the attraction between particles over the region, where the number of chemisorbed water molecules is insufficient to compensate for electrostatic charges on the surfaces that have been freshly formed on grinding; second, because of a drastically facilitated processes of recrystallization of particles under conditions when the interface is free from a layer of alien atoms and molecules. The particles are attracted maximally tightly to one another and since there are no any steric difficulties at the boundary, they merge in a single whole under the influence of impulses of pressure and temperature that are generated upon the impacts in a planetary mill. The effect becomes weaker as the surface is humidified.

Thus, the minimal size of particles of α - Al_2O_3 nanopowder is attained owing to the inhibited process of recrystallization and owing to the associated shift in the position of the dynamic equilibrium that is described in

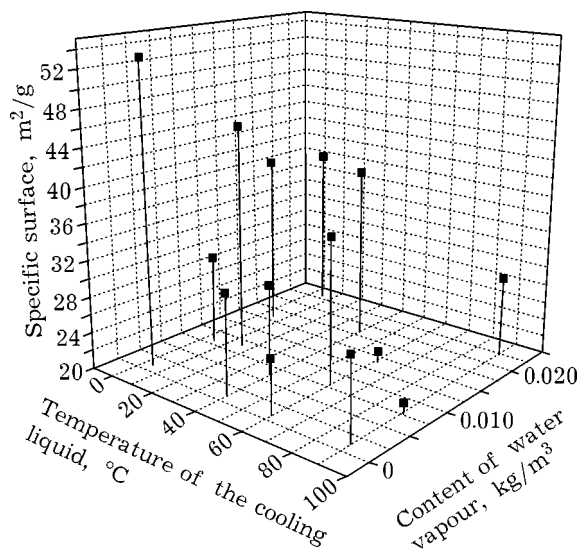


Fig. 6. Dependence of specific surface of the generated α - Al_2O_3 nanopowders on the activator cooling temperature and on the content of water vapour inside the activator.

[3]. Upon a subsequent increase in the quantity of molecules that are adsorbed on the surface of the particles, the adhesion develops and becomes more intensive in the course of time due to capillary attraction forces. These forces facilitate the formation of aggregates that become exactly the site of recrystallization of the crystallites and their size rises owing to the recrystallization. It is apparent that the efficiency of grinding drops in the field of increased water content because of weakening of adhesion and slip of particles relative to each other.

If the above assumption on the nature of the minimum in the curve of Fig. 5 is true, then the powders not only with a minimal size of crystallites, but also with no strong aggregates must be generated in this region. Figure 6 displays a plot of specific surface of α - Al_2O_3 nano powders that are generated upon hyperfine grinding *versus* the temperature of a liquid to cool the barrels and *versus* the content of water vapour in the atmosphere of the barrel.

Upon a comparison of Figs. 3 and 5, it is evident that the regions of experimental conditions that are associated with obtaining of powders with a minimal size of crystallites and powders with a maximal specific surface are approximately coincident. Hence, powders with a slightly aggregated structure are really formed in the investigated field. Meanwhile, a character of the dependence is more complex than that

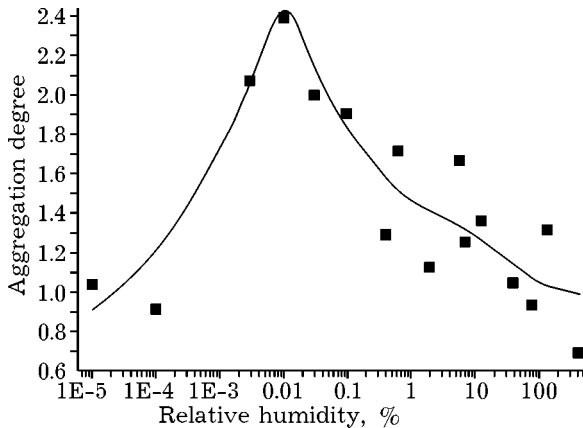
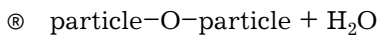
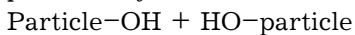


Fig. 7. Aggregation degree as a function of the relative humidity in the activator.

might be expected based on the assumption that the more finely the powder, the more its specific surface. At a high temperature of the cooling liquid and consequently, at a higher temperature in the barrel, the values of specific surface are significantly less than those calculated with the formula (1), which is related, probably, to the aggregation as a result of strong chemical bonds formed between the particles by the reaction



Specific surface of powders drops on their aggregation and consequently, the size of particles or aggregates (d_p) that is calculated with the formula (3) becomes larger than the size of crystallites (d_c) that is determined for the same powder. A ratio $N = d_p/d_c$ can be taken as the aggregation degree of the powder. Figure 7 displays the dependence of N on the

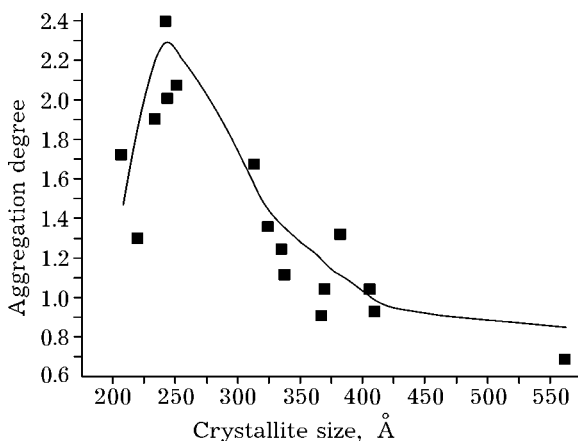


Fig. 8. Aggregation degree as a function of the size of crystallites.

relative humidity in the mincing barrel. The dependence also shows a distinct extremum, since an average size of particles of the powder in this field is greater. However, as would be expected, from the most obvious assumption that the tendency for clustering increases with a decrease of particle size it follows that a maximum in Fig. 7 must be arranged at the same values of the relative humidity, as the minimum in Fig. 5. Actually, its position is shifted by more than an order of magnitude to the region of small values. Figure 8 displays this fact still more distinctly.

Hence, in the field of values of the relative humidity that is arranged between the extremums of the curves in Figs. 5 and 7, a mechanism exists that is responsible for strengthening of the aggregation of particles and for the formation of strong aggregates upon grinding that do not destruct upon the subsequent acidic treatment. The results of the research demonstrate that the amount of water in the atmosphere in this field is so small that it would suffice to cover only 1 % of the area of the nanopowder even in the case of 100 % adsorption of molecules on its surface. Thus, one might expect here that a significant electrostatic interaction occur between the particles of the powder and the interaction leads to the attraction of surfaces that are practically free from the adsorbed molecules and to the formation of strong conglomerates of particles that do not break up in acid. Consequently, the shift of the maximum in Fig. 7 relative to the minimum in Fig. 5 is additional evidence in favour of the critical impact of electrostatic forces on the emergence of the extremum in the curve of Fig. 5.

CONCLUSIONS

Intensive mechanical treatment of $\alpha\text{-Al}_2\text{O}_3$ in planetary mills gives rise to a powder that is made up of nanometer (200–400 Å) range crystallites. Treatment of the powder with muriatic acid causes its disaggregation and substantial growth of its specific surface. The size of the generated crystallites represents an extremal function on the relative humidity in the atmosphere of the mincing barrels. There

exists a range of the values of relative humidity, wherein the finest (200 Å) and slightly aggregated powders can be obtained. The extremal character of the dependence is possibly related to the intensification of recrystallization processes for nanocrystallites in strongly linked aggregates due to appreciable electrostatic attraction between surfaces that are free from adsorbed molecules.

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