

RESEARCH IN THE AREA OF PREPARING ACTIVATED ALUMINA. PART 4. NEW TECHNOLOGICAL APPROACHES FOR SYNTHESIS OF ULTRAFINE α -Al₂O₃¹

M. A. Trubitsyn,^{2,4} N. A. Volovicheva,^{2,5} L. V. Furda,² V. V. Lisnyak,²
A. P. Kurbatov,² V. I. Kuzin,³ and N. A. Morozova³

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Results of new integrated technological approaches to synthesis of ultrafine α -alumina using commercially available metallurgical alumina as a raw material are presented. The effect of seven different modes for calcination of the initial γ -Al₂O₃ in the temperature range 1200 – 1600°C is studied. It is revealed that experimental regimes determine the size of the primary crystals and milling capacity of firing products. It is established that by varying temperature regimes it is possible to obtain intentionally both monomodal and multimodal powders.

Keywords: reactive alumina, synthesis, dispersion, grain size composition, fine powders, ball mill.

INTRODUCTION

In recent years finely dispersed activated α -Al₂O₃ (reactive alumina) has been used extensively as a very fine component during manufacture technical and special corundum ceramics and as a matrix system component in low-cement refractory cast mixes technology [1 – 3].

Within reactive alumina material is dispersed to primary sizes (0.3 – 2 μ m) and a significant proportion of particles has a submicron size, i.e., less than 1 μ m (up to 90%). For mass production of fine and ultrafine activated α -Al₂O₃ there is currently use as a rule of calcined alumina. This alumina is prepared by heat treatment (calcination) of Bayer aluminum hydroxide from 1300 to 2000°C [4 – 6]. The heat treatment regime for the original material has an effect on the size of α -Al₂O₃ crystals formed and in fact heating and cooling rate, and also isothermal exposure. The higher the calcining temperature the larger is the size of pore-free primary crystals and Al₂O₃ content in α -form.

In turn thermal history has a marked effect on structure and morphological characteristics and capacity for milling calcine aluminum oxide. In existing industrial production regimes reactive alumina as a commercial product is as a rule prepared by mechanical dry or wet milling of alumina raw material in the form of α -Al₂O₃ to primary pore-free crystals (single crystals) [4, 7 – 9]. The main technical properties of reactive alumina may concern: diameter D_{50} (size in microns below which the product contains 50% of particles), modality of grain distribution and also finished powder specific surface. Currently the main volume of large tonnage industrial production of reactive alumina of various grades is concentrated overseas. In addition important tasks are organization of domestic production of similar products and also a search for new approaches to preparing submicron activated aluminum oxide.

Even in 1967 A. Pearson [10] described a method for preparing activated alumina by dry milling in a ball mill using additive-intensifiers based upon single monatomic (ethanol, methanol, isopropanol, n-propanol, n-octanol) or multiatomic (ethylene glycol, triethylene glycol) alcohols, and also with use of compounds of the amine group (mono- and tetra-ethanoalamine) or complex esters (n-butyl acetate). It has been demonstrated that introduction of this type of additive prevents particle aggregation and achievement of a critical level of fineness (2 – 3 μ m) and reduces milling dura-

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² Belgorod State National Research University, Belgorod, Russia.

³ ZAO PKF NK Saryi Oskol, Russia.

⁴ trubitsn@bsu.edu.ru

⁵ volovicheva@bsu.edu.ru

tion. However, the proposed method has not found practical application in view of the use of quite high concentrations of additive-intensifiers, i.e., 0.5 wt.% which gives rise to an increase in reagent consumption under multitonnage production conditions.

The authors of publication [11] have proposed a method for preparing submicron aluminum α -oxide powder, including preliminary treatment of Bayer aluminum hydroxide in ball mill with simultaneous introduction of a certain amount of α - Al_2O_3 as a primer. Milling products were calcined at 1350 – 1540°C and subjected to milling within an organic solvent. The alumina powder obtained consisted of aluminum α -oxide particles of spherical shape with monomodal distribution in the range 0.1 – 0.3 μm . These very fine powders are proposed for use in technology for preparing dense corundum ceramic. However, this method is not widespread in multitonnage production of activated alumina due to production complexity.

On the whole the amount of information sources devoted to various methods for preparing reactive alumina is extremely limited or unavailable. In the present article results are provided for research in the field of new economically effective approaches to preparing submicron active aluminum oxide with controlled structural and morphological properties.

RESEARCH PROCEDURE

The starting material for preparing activated aluminum α -oxide is commercially available metallurgical alumina G-0 (Al_2O_3 content 98.6 wt.%). With respect to mineral composition G-0 is predominantly γ - Al_2O_3 crystalline phase. Alumina raw material was subjected to preliminary milling in a ball mill in the presence of an organic additive, i.e., milling intensifier. Then the milled material was compacted into briquettes and heat treated in the range 1200 – 1600°C by a specially developed regime: regime 1 ($T = 1200 - 1250^\circ\text{C}$); regime 2 ($T = 1250 - 1350^\circ\text{C}$); regime 3 ($T = 1350 - 1450^\circ\text{C}$); regime 4 ($T = 1450 - 1500^\circ\text{C}$); regime 5 ($T = 1550 - 1600^\circ\text{C}$); regime 6 ($T = 1450 - 1550^\circ\text{C}$), regime 7 ($T =$

1500 – 1550°C). Calcination products were crushed and then subjected to fine milling within a laboratory ball mill by a special production regime provided in publication [12].

Physicochemical properties of the original alumina raw material and calcination products were studied by analytical scanning electron microscopy (Quanta 200 3D and Quanta 600 FEG, FEI, Netherlands) and x-ray phase analysis (diffractometer Ultima IV, Rigaku, Japan). The grain size composition was determined in a Microtrac S3500 (Microtrac Inc., USA) particle analyzer by a laser diffraction method. Water was used as a dispersing medium. Powder specific surface was determined by the low-temperature adsorption and thermodesorption of nitrogen (TriStar II 3020, Micromeritics, USA) method.

The grain size composition for the original alumina (G-0) and its preliminary milling products is shown in Fig. 1. With respect to dispersed composition the original grade G-0 alumina is monomodal with a maximum in the region of 100 μm (see Fig. 1a). The median particle diameter is 90 μm . However during milling within the product there is formation of modes that it is difficult to differentiate in the range 1 – 4 μm (see Fig. 1b). The second maximum is recorded more clearly and it is located in the range 20 – 30 μm . In this case the median particle size is of the order of 10 μm .

In SEM pictures alumina of alumina G-0 individual spherulites with a size of 80 – 150 μm are clearly differentiated (Fig. 2a), represented by densely packed globules of prismatic particles. At high magnification (Fig. 2b) within the spherulite structure slotted pores are clearly differentiated, formed due to growth of plate-shaped primary crystals.

After milling alumina two types of particles are recorded within SEM pictures differing not only in morphology, but also in size (Fig. 2c). The first type forms volumetric aggregates, whose microstructure is identical to that shown in Fig. 2a. However, in contrast to the original alumina raw material the size of these aggregates is smaller, i.e., of the order of 50 – 70 μm , and they have an irregular shape since they are the results of spherulite breakage during milling. The second group of particles is represented by isometric platelets with a size from fractions to 3 – 5 μm , which are distributed

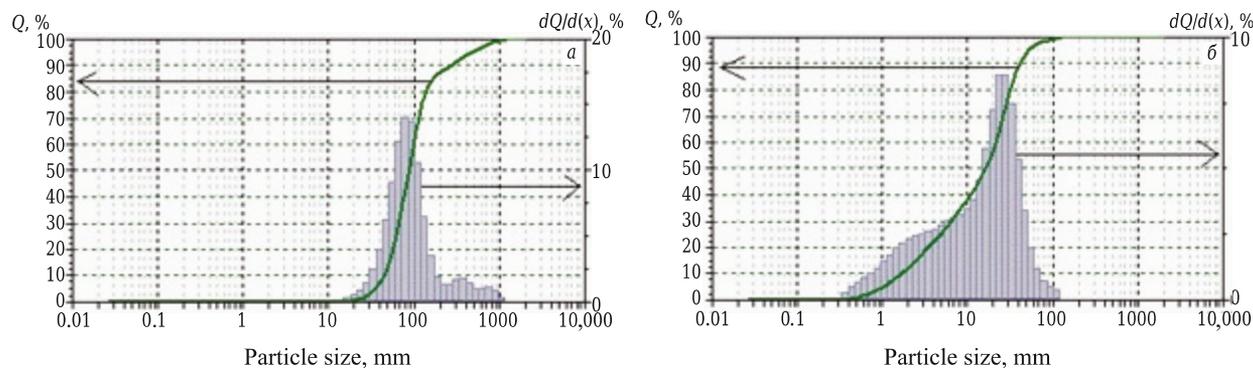


Fig. 1. Particle size distribution: a) original metallurgical alumina; b) alumina after preliminary milling.

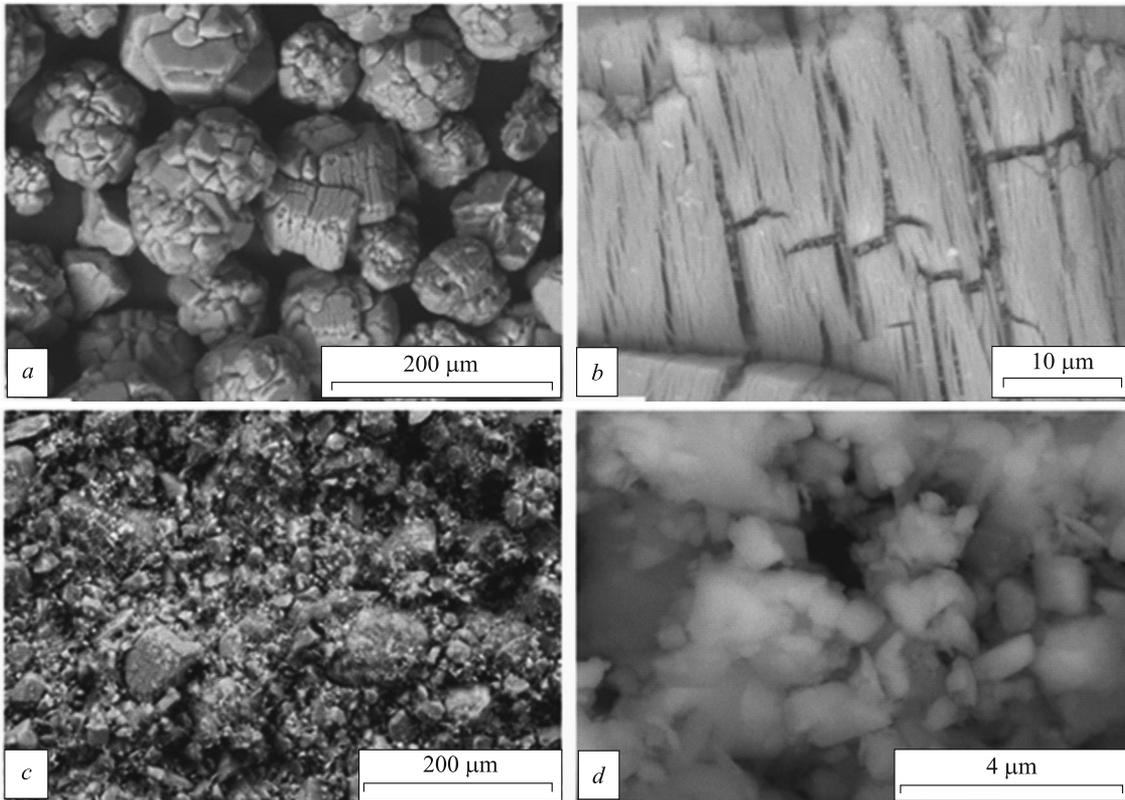


Fig. 2. Alumina raw material grain morphology: *a, b*) original alumina G-0; *c, d*) alumina after preliminary milling.

uniformly between coarser aggregates. At higher magnification (Fig. 2*d*) it is revealed that finely dispersed particles have a different shape: there is typically presence not only of sharp angles, but also rounded plates.

According to x-ray phase analysis data the mineral composition of the product, calcined above 1200°C, independent of heat treatment regime is represented by α -alumina (Fig. 3). The effect of heat treatment regime for the original

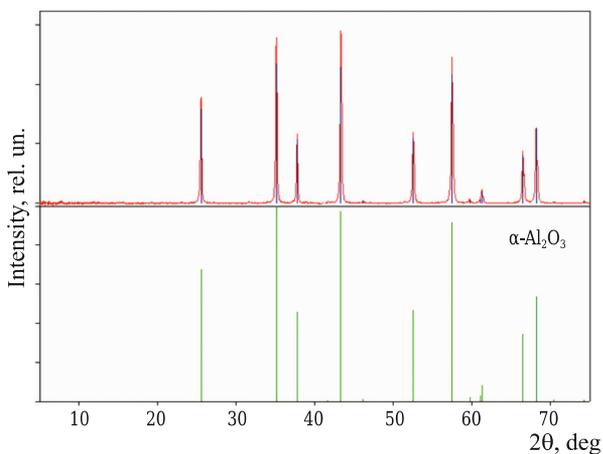


Fig. 3. Typical powder diffraction pattern for products of calcined alumina G-0 above 1200°C.

alumina on structural and morphological properties of synthesized α - Al_2O_3 has been evaluated by scanning electron microscopy (Fig. 4).

As is seen from SEM pictures, with a calcining temperature of 1200 – 1250°C (regime 1, Fig. 4*a*) formation of ultrafine plate-shaped crystallites is observed with predominant size of 0.1 – 0.3 μm . Also present are layered agglomerates of irregular shape with sizes of 2 – 4 μm . It is proposed that this type of agglomerate is fragments of spherulites of the original metallurgical alumina unbroken during milling (see Fig. 2*a*). In SEM pictures obtained at maximum magnification within the interlayer space of these alumina agglomerates it is possible to observe submicron single crystals of α - Al_2O_3 .

With a calcining temperature of 1250 – 1350°C (regime 2) there is marked increase in the α - Al_2O_3 crystallite size to 0.3 – 0.4 μm (see Fig. 4*b*). Particles comprising powders are thin strongly agglomerated platelets of isometric shape with rounded edges.

Heat treatment of alumina raw material in the range 1350 – 1600°C using regimes 3, 4, and 5 leads to further crystallite coarsening (see Fig. 4*c – e*), it has been revealed that during growth primary Al_2O_3 crystals are transformed into a volumetric spherical shape. With application of regime 4 the dimensions of alumina particles reaches 0.6 – 0.8 μm , and subsequent refinement makes it possible to obtain almost

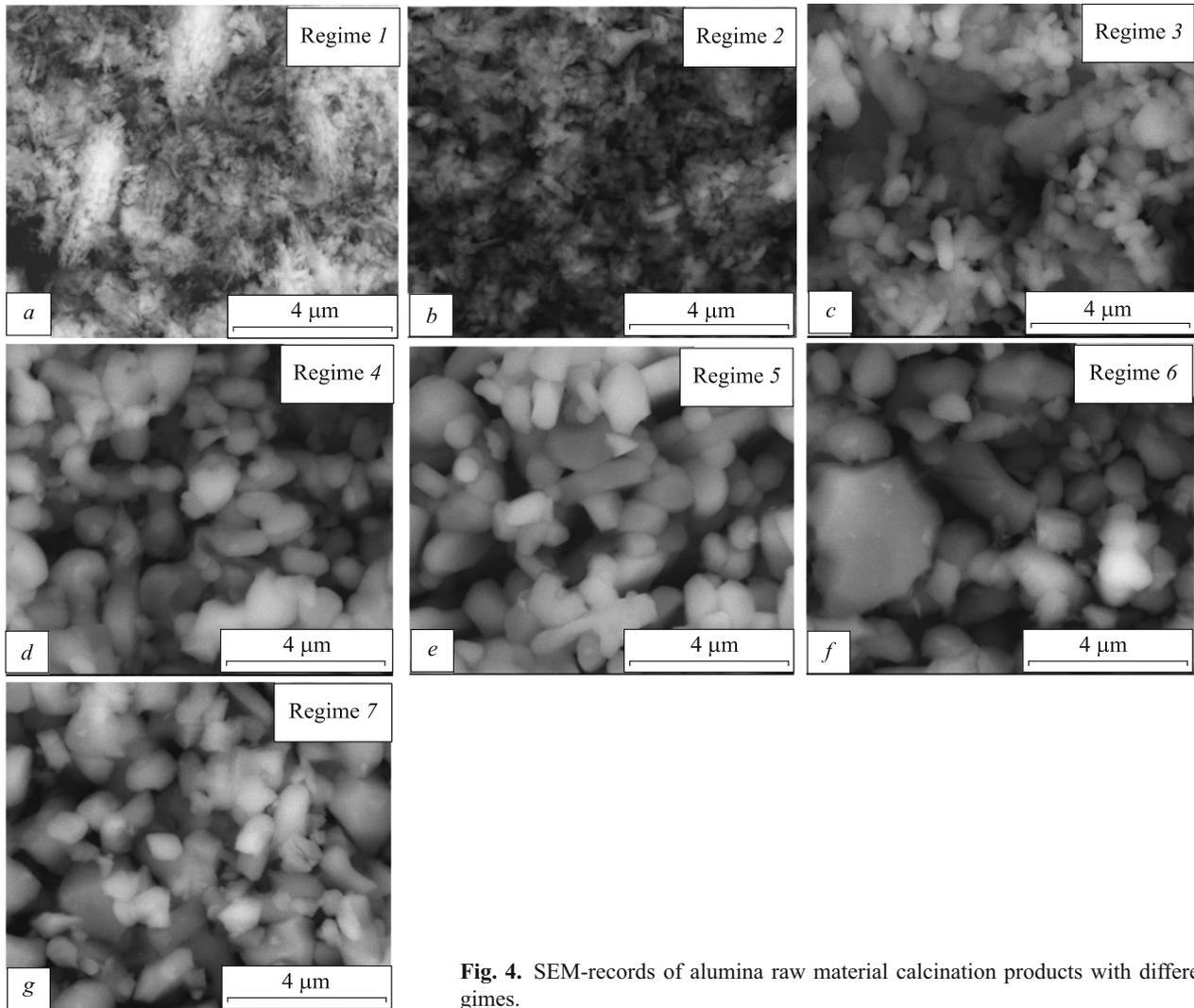


Fig. 4. SEM-records of alumina raw material calcination products with different regimes.

unagglomerated powder (see Fig. 4*d*). The greatest primary aluminum α -oxide largest crystal size (1.1 – 1.5 μm) was obtained by regime 5 with firing in the range 1550 – 1600°C.

Calcination of the original metallurgical alumina with use of regimes 6 and 7 made it possible to obtain products with two types of morphological primary crystals (see

Fig. 4*f, g*). The first type may be related to prismatic particles with clearly formed boundaries. The size of these crystals varies within the limits from 1 to 3 μm . The second type form platelets of both rounded and irregular sharp-angle shape with size up to 0.5 μm .

TABLE 1. Alumina Raw material Firing Products Textural Characteristics

Regime	Temperature range, °C	D_{20} , μm	D_{50} , μm	D_{90} , μm	Submicron fraction (<1 μm), % content	S_{sp} (BET), m^2/g
1	1200-1250	0.61	1.68	13.4	36.2	5.55
2	1250-1350	0.52	1.29	9.82	43.5	2.82
3	1350-1450	0.45	0.67	2.22	69.5	2.41
4	1450-1500	0.49	0.79	2.56	62.5	2.00
5	1550-1600	0.48	0.78	2.62	62.5	1.72
6	1450-1550	0.76	1.75	7.28	30.2	1.20
7	1500-1600	0.75	1.73	5.71	30.3	1.15

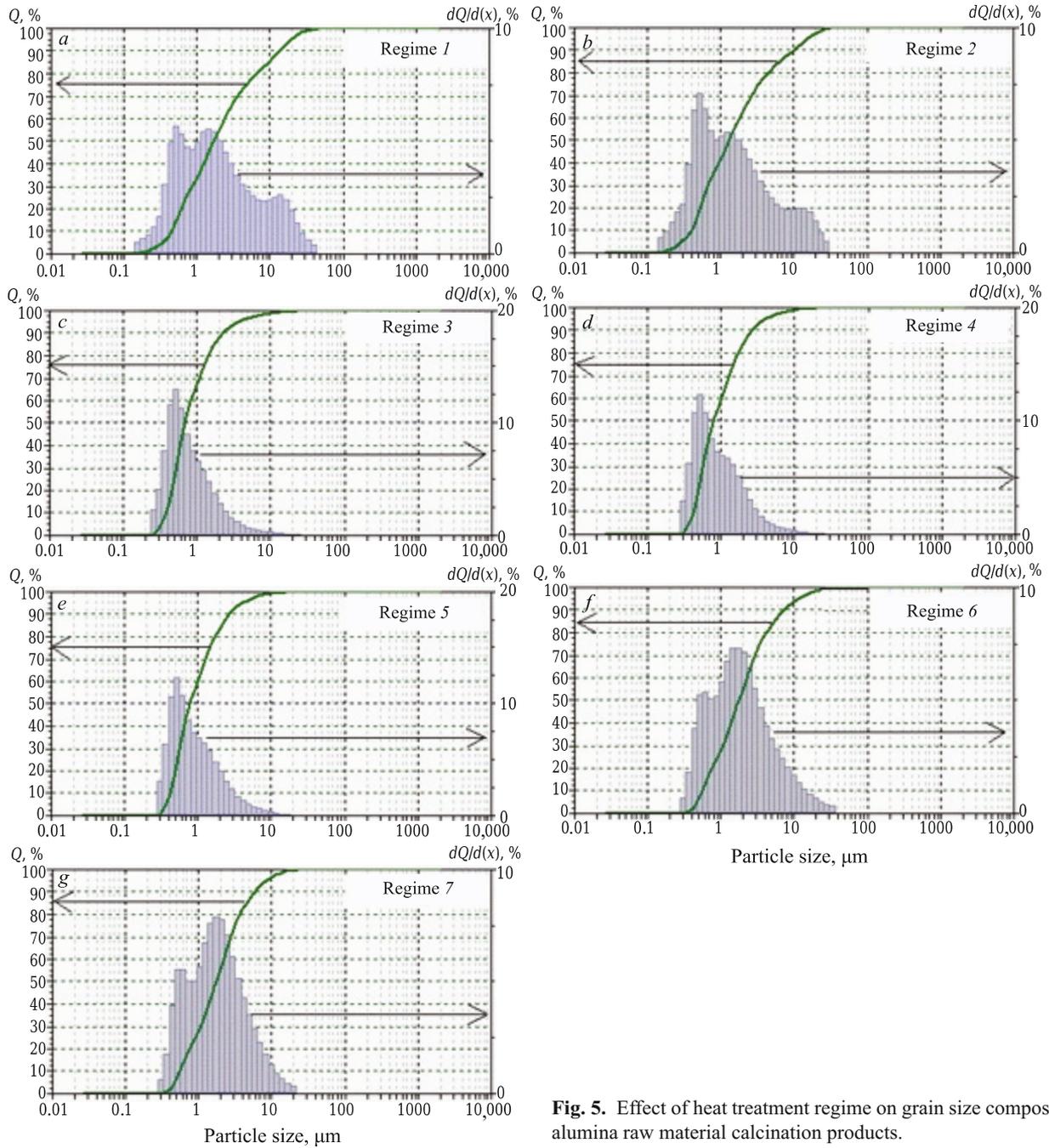


Fig. 5. Effect of heat treatment regime on grain size composition of alumina raw material calcination products.

Integral curves and particle distribution diagrams are shown in Fig. 5 within products of milled α -alumina obtained with different firing regimes. Subsequent milling of calcination products by regimes 1 and 2 made it possible to obtain a three-modal grain size composition with maxima 0.5 – 0.6, 1 – 2, and 10 – 11 μm respectively (see Fig. 5a, b). The polymodal nature of the products obtained is a consequence of intentional agglomeration of ultrafine crystallites, which was confirmed by results of powder electron microscope analysis.

Synthesis of α -alumina in a relatively low temperature region 1350 – 1600°C, which is accomplished by regimes 3 – 5, made it possible to obtain powder with a stable tendency towards monomodal grain distribution. According to particle distribution histograms for these powders there is typically presence of a single maximum in the region 0.5 – 0.6 μm (see Fig. 5c – e). These experimental results are in good agreement with the electron microscope analysis data, which clearly demonstrate formation within a system of individual microcrystallites with approximately identical dimensions, (see Fig. 4c – e).

During calcination by regimes 6 and 7 powder products form a bimodal grain size composition (see Fig. 5f, g). The maximum of the first mode was recorded in the range 0.5 – 0.6 μm , and the second in the range 1 – 2 μm . This is a consequence of forming two types of primary crystallites during calcination by the abovementioned regime (see Fig. 4f, g).

In the concluding stage of the work the main textural characteristics of finished products of activated aluminum α -oxide were studied: specific surface, porosity, and ratio of the content of coarse medium, and fine fractions (D_{90} , D_{50} , and D_{20} respectively). Comparable results of experimental studies are in Table 1.

It follows from Table 1 that texture properties of the milled alumina products are determined by thermal history and in fact calcination regime. With regimes 1 and 2 a greater specific surface is noted up to 5.5 m^2/g . in addition, D_{50} does not exceed 1.7 μm and the content of submicron fractions is within the limits 36 – 44%. In our opinion this is connected with a significant proportion within a powder system of ultrafine α - Al_2O_3 crystallite agglomerates.

With regimes 3, 4, and 5 the submicron fraction content in all three of these powders is more than 69%, and the median particle size is 0.7 μm . An increase in primary pore-free crystal size leads to a reduction in alumina specimen specific surface.

Use of regimes 6 and 7 makes it possible to obtain bimodal powder with comparable texture properties, and in fact with a median particle size of 1.73 – 1.75 μm , submicron fraction content 30% and specific surface 1.15 – 1.20 m^2/g .

CONCLUSION

Results are presented for a new comprehensive approaches to synthesizing finely dispersed activated α -alumina. Seven production regimes for heat treatment of available metallurgical alumina in the range 1200 – 1600°C have been studied.

Analysis of SEM pictures of products prepared with different regimes makes it possible to reveal a stable trend towards an increase in α - Al_2O_3 primary crystal size with a changeover into a high temperature region for original material heat treatment. The possibility has been demonstrated of controlling these structural and morphological properties of α -alumina single crystals in relation to thermal history. The temperature regimes developed make it possible to obtain primary crystallites both of lamellar form and also in the form of volumetric prismatic pore-free particles.

It has been revealed that experimental regimes give rise to the size of crystals and the capacity of fired product for milling. The products obtained have a submicron fraction content from 30 to 70% and specific surface from 1.15 to 5.55 m^2/g .

It has been established that by varying temperature regimes it is possible intentionally obtain both bimodal and also multimodal powders.

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