

RESEARCH IN THE AREA OF PREPARING ACTIVATED ALUMINA. PART 2. EFFICIENCY OF PREPARING FINELY DISPERSED ALUMINUM OXIDE POWDER USING A BALL MILL¹

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Results of studying preparation of activated finely dispersed alpha-alumina by dry milling in a ball mill are presented. The α -Al₂O₃ refinement mechanism is considered. It is shown that the powder material obtained has properties comparable with similar commercial products of domestic and overseas producers.

Keywords: reactive alumina, dispersion, particle size distribution, fine powders, ball mill, grinding kinetics.

INTRODUCTION

Currently both overseas and within Russia there is extensive propagation of a new generation heat engineering composite refractory materials known as low-cement castables (LCC) [1]. They are based on use of fundamentally new functional fine matrix systems containing a limited amount of specialized hydraulic binders, mainly calcium aluminate cements with a high aluminum oxide content (>70%), and also very fine mineral composites. In spite of the fact the proportion of these components within refractory composite is only 25 – 35%, nonetheless a fine matrix has a decisive effect on castable rheology, convenience in laying, setting time, strength, and operating properties [2 – 7]. As a consequence an important task is optimization of the grain size composition not only for coarse grained filler but also very fine matrix components.

Recently matrix systems for low-cement refractory mixes using finely dispersed active aluminum oxide have been developed and successfully approved under industrial conditions. Among important technical engineering advantages of finely dispersed alumina is not only an improvement of production properties for refractory castables, but also for-

mation of a dense ceramic matrix with a reduction in sintering temperature and also absence of readily-melting eutectics. This makes it possible to prepare heat engineering composite materials with good operating properties [8 – 10].

The main raw material for producing reactive alumina is calcined aluminum oxide. This product is obtained by firing (calcining) Bayer aluminum hydroxide above 1200°C. The α -alumina crystallite size formed depends on thermal history and varies normally from 0.5 to 5 μ m. The higher the calcining temperature, the greater is the dense primary crystal size and aluminum oxide content in α -form [11].

During production of finely dispersed active aluminum oxide calcined alumina is dispersed in order to break down porous spherulites and to reduce their size to primary crystals. In this case of particular importance is the selection of active milling unit and organization of the optimum milling regime in order to achieve the required fine product properties. Such milling units should provide economic fine milling of solid mineral materials. During milling there should be no contamination of finished product with undesirable admixtures, containing iron, silicate components, etc.

Recently in order to prepare finely dispersed mineral powders various types of milling units are used, for example vortex, jet, or vibration mills [12]. However, more simple, economic, and widespread are drum ball mills [13, 14]. The efficiency of milling in ball mills and energy consumption depend upon their rotation frequency and also on milling body intensity, shape, and size. In order to avoid undesirable

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impurities it is expedient to use wear-resistant milling bodies and drum mills lined with high-alumina or wear-resistant resin pastes. However, during dry milling in periodically operating mills there is material lump formation after reaching a critical particle size ($2 - 3 \mu\text{m}$) and as a consequence subsequent milling slows down considerably.

The aim of the present work is to study the efficiency of preparing finely dispersed activated α -alumina by dry milling in a ball mill.

RESEARCH PROCEDURE

In order to prepare finely dispersed powder material the model starting material used was calcined alumina grade Nabalox NO 105 from Nabaltec AG, Germany. An ML-1 ball mill with drum made of high-alumina porcelain with a working volume of 2 dm^3 was used for milling specimens. The drum working rotation frequency was 100 rpm. The milling bodies used were corundum cylindrical pebbles with an average diameter and length of 20 mm. the milling charge comprised 25% of the drum working volume. Optimum production parameters for preparing finely dispersed $\alpha\text{-Al}_2\text{O}_3$ with use of a ball mill have been described in publication [14].

Kinetic dependences for milling were studied by analyzing the fine powder composition after each 2 h of milling with prescribed production parameters. In each stage of the study integral curves and particle size distribution histograms were obtained using a Microtec S3500 (USA) laser analyzer.

Physicochemical properties of specimens of the original Nabalox NO 105 alumina and its milling products were studied by analytical scanning electron microscopy (SEM, FEI Quanta 200 3D and Quanta 600 FEG, Netherlands), thermogravimetric (SDT Q 600, USA), and x-ray phase analyses (XPA, Ultima IV diffractometer, Rigaku, Japan). Powder material elementary composition was established by x-ray micro-analysis using a Quanta-200 3D scanning electron microscope together with an energy-dispersion EDAX x-ray detector. Powder specific surface and porosity were determined by a low-temperature absorption method and ther-

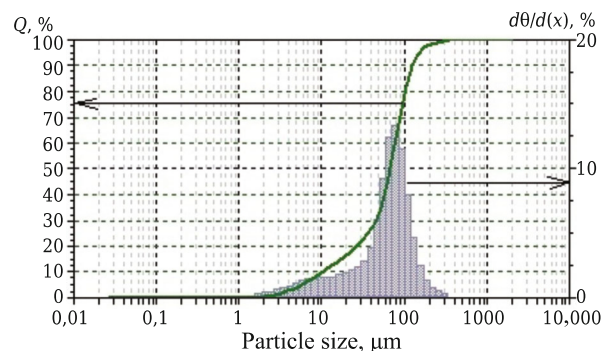


Fig. 1. Integral curve and particle size distribution histogram of Nabalox NO 105 alumina with respect to size.

mal desorption of nitrogen (automated equipment TriStar II 3020, Micromeritics, USA).

RESULTS AND DISCUSSION

The original high-alumina raw material Nabalox NO 105 is a polydispersed white powder with average milling capacity. It is quite readily dispersed in distilled water and no tendency is observed towards particle aggregation within an aqueous medium. A unique maximum within a Nabalox NO 105 alumina specimen histogram (Fig. 1) is observed in the range $60 - 70 \mu\text{m}$; the proportion of particles of this size is a little more than 13%. On the whole high-alumina material exhibits average fineness with a median particle diameter of about $70 \mu\text{m}$ (see Fig. 1).

According to chemical analysis data Nabalox NO 105 the Al_2O_3 content is in an amount of 99.57 wt.%; also recorded is presence of Na_2O (0.30 wt.%) and silicon and iron (III) oxides in an amount of 0.002 and 0.003 wt.% respectively. According to XPA data a Nabalox NO 105 alumina specimen is predominantly crystalline $\alpha\text{-Al}_2\text{O}_3$ phase (not less than 98%).

In SEM pictures for original alumina (Fig. 2) granular aggregates are observed with sizes $60 - 80 \mu\text{m}$, composed of individual crystals of two types: lamellar shape (platelet size $3 - 4 \mu\text{m}$) and spherical shape (average size $0.5 \mu\text{m}$).

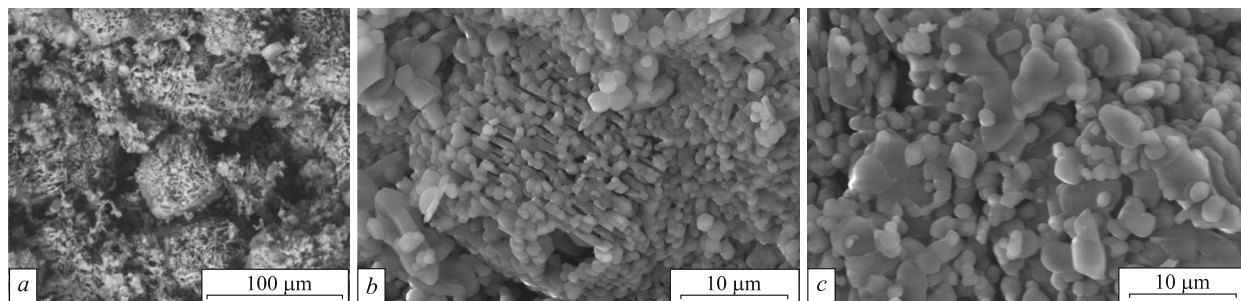


Fig. 2. Original Nabalox NO 105 alumina SEM-pictures at different magnification.

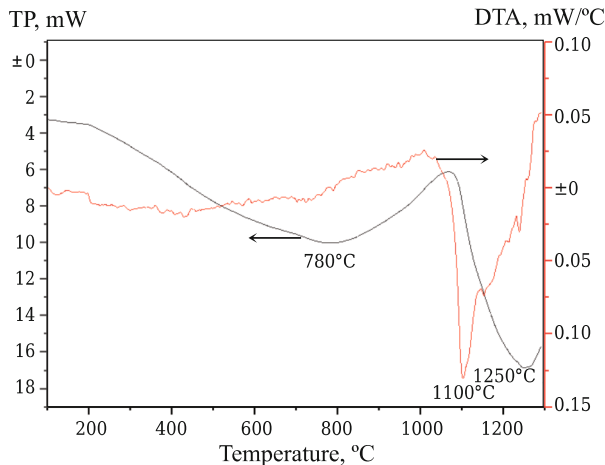


Fig. 3. Original Nabalox NO 105 alumina TP and DTA curves.

A spherulitic grain structure is clearly seen formed due to growth of a considerable number of individual elements, i.e., primary crystallites [15, 16]. Pores in this case are cavities between growing particles. The piled up nature of the layout of flat Al_2O_3 crystals should be noted as a result of which slot-like pore spaces arise. The solid carcass and pore space are interconnected and form a single morphological system. Ultrafine particles of are distributed irregularly among coarse platelets. The lamellar crystals themselves have an irregular shape with rounded or sharp edges extended in side projection to 2 μm and with thickness of several fractions of a micron.

TP and DTA curves for the original high-alumina raw material are shown in Fig. 3. On a DTA curve an endothermic effect is observed at 1100°C that may be connected with polymorphic transformation of alumina impurity phases by the scheme: $\chi\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$.

In order to reveal features of the change in powder fine composition of Nabalox NO 105 alumina process kinetics were studied under prescribed production conditions. Sample selection was performed each 2 h. In order to evaluate the nature of change in milled material content of coarse, average, and fine fractions indices D_{90} , D_{50} , and D_{20} relating to particle size below which 90, 50 and 20% of fired product are found respectively. Kinetic milling curves are shown in Fig. 4.

Analysis of Fig. 4 shows that the fastest milling rate is observed in the first 2–3 h. In this period there is active crushing of coarse granular aggregates into components that are connected weakly with each other and may be broken down by impact mechanical action [16]. Subsequently after 24 h of milling this refinement mechanism changes and the effect of wear starts to predominate. Presence of shears and microcracks at the surface of particles facilitates an increase in the proportion of finely dispersed product and submicron fractions. With the prescribed production parameters finely

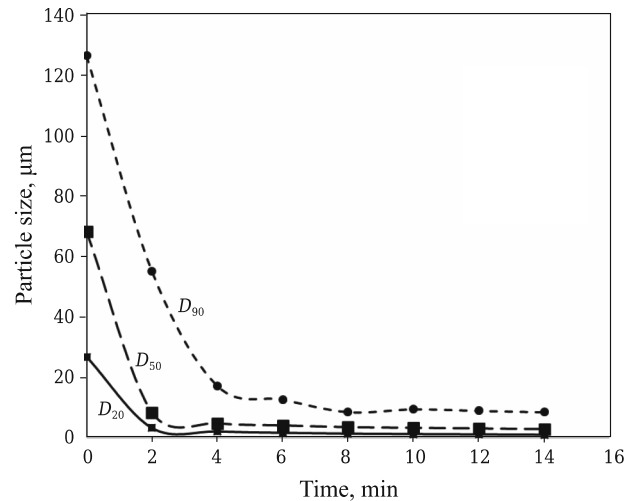


Fig. 4. Nabalox NO 105 alumina refinement kinetic curves for three dispersed fractions.

dispersed powders were obtained a medium particle diameter D_{50} less than 3 μm and a submicron fraction content of 19% already after 12 h. Emergence of curves into plateau points to completion of the spreading mechanism of milling body activity and complete transfer of the milling process into the wear phase. In this case the average fine fraction size D_{20} decreases by more than a factor of 27 and corresponds to the size of submicron fractions ($<1.0 \mu\text{m}$) already after 8 h of milling; D_{90} for a similar time period was 8.0–9.0 μm .

During milling high-alumina material formation of particle bimodal distribution was detected within products. On a

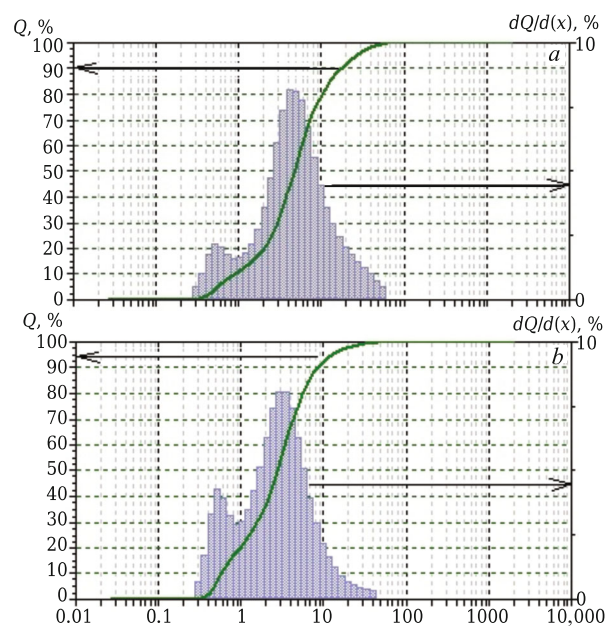


Fig. 5. Nabalox NO 105 alumina particle size distribution integral curve and histogram: a) after 4 h grinding; b) after 14 h grinding.

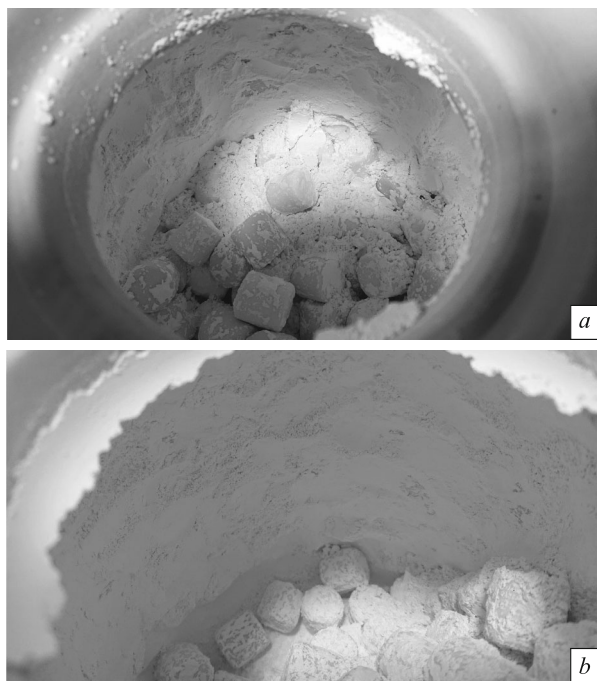


Fig. 6. Nabalox NO 105 alumina grinding products in ball mill: *a*) after 4 h grinding; *b*) after 14 h grinding.

particle distribution histogram already after 4 h of milling Nabalox NO 105 alumina (Fig. 5*a*) two modes are recorded with particle sizes of 0.5 and 4.4 μm . In this case with an increase in milling duration the bimodal nature of particle distribution is retained (Fig. 5*b*). This may be explained by structural morphological features of the original alumina raw material within which two types of primary crystals are present. SEM data (see Fig. 2) are in good agreement with results of determining the material grain size composition confirming the bimodal nature of particle distribution. It should be noted that the polymodality facilitates greater packing density that improves castable rheological properties [1, 9, 17].

In addition, a tendency is observed for particles towards agglomeration after 6 h of milling ($D_{50} = 3.9 \mu\text{m}$). After 14 h of milling a high degree of powder lumpiness and sticking to mill walls and pebbles was detected ($D_{50} = 2.7 \mu\text{m}$) that complicated unloading of finely dispersed product (Fig. 6).

A feature of powders prepared by the dry milling method in balls mills is the effect of their aggregation on reaching a

fineness level of less than 3 μm . In this case there is formation of molecular dense aggregates (“friction welding”) [1]. An effective technological solution to this problem is use of an additive, i.e., milling intensifiers of various types whose action is traditionally explained by a theory of absorption reduction of solid strength described in the A. P. Rebinder effect [18]. Currently Russian and overseas manufacturers produce commercial milling intensifiers. As a rule they are based on compounds of a group of amines (triethanol amine, tri-isopropanol amine), glycols (diethylene glycol, polypropylene glycol), and surfactants (lignosulfonates, sodium polymethyl sulfonate, polycarboxylates) [19]. Establishment of the effect of this type of additives on the process of preparing finely dispersed activated α -alumina is of significant practical and scientific interest and will be a subject of our subsequent research.

Important production properties for very fine powder material are apparent density in loose and compacted conditions, natural repose angle, moisture content, and loss during calcining. Values of these parameters for active α - Al_2O_3 obtained by milling the original raw material for 14 h: apparent density in a loosely compacted condition and correspondingly 0.62 and 0.88 g/cm^3 , natural repose angle 73 deg, moisture content 0,15 wt.%, Δm_{cal} 0.32 wt.%.

In the concluding stage of work textural and morphological properties were determined for finished finely dispersed activate aluminum oxide: specific surface, porosity, and the ratio of the content of coarse D_{90} , average D_{50} , and fine D_{20} fractions (see Table 1, Fig. 7).

It is seen from Table 1 that the properties of finely dispersed products obtained by the authors of the present article and commercial analogs are comparable. In particular an almost identical particle median diameter is observed. However, D_{90} for a specimens grade GRT is approximately twice as high as that for a specimen prepared by the authors. This may be connected with the different thermal history of the starting raw materials. Reactive alumina grade CT-22 is distinguished by a very high fineness and as a consequence a developed specific surface, but in this case it has a median particle diameter comparable with the product obtained. SEM pictures for finely dispersed activated aluminum oxide prepared by dry milling of alumina for 14 h are shown in Fig. 7. It is seen that within the material there are individual

TABLE 1. Texture Properties Obtained for Finely Dispersed α - Al_2O_3 Compared with Similar Commercial Products

Specimen	S_{sp} (BET), m^2/g	Overall pore volume, mm^3/g	Pore size, nm	Particle size, μm			Submicron fraction content ($\leq 1 \mu\text{m}$), %
				D_{20}	D_{50}	D_{90}	
Activated α - Al_2O_3 (14 h grinding)	0.84	2.1	10.58	0.96	2.77	8.42	20.5
GRT (Borovich Refractory Combine)	1.11	2.3	8.94	0.91	2.52	18.35	21.2
CTC-22 (Atlantis Company)	2.26	5.7	10.28	0.65	2.17	8.70	25.6

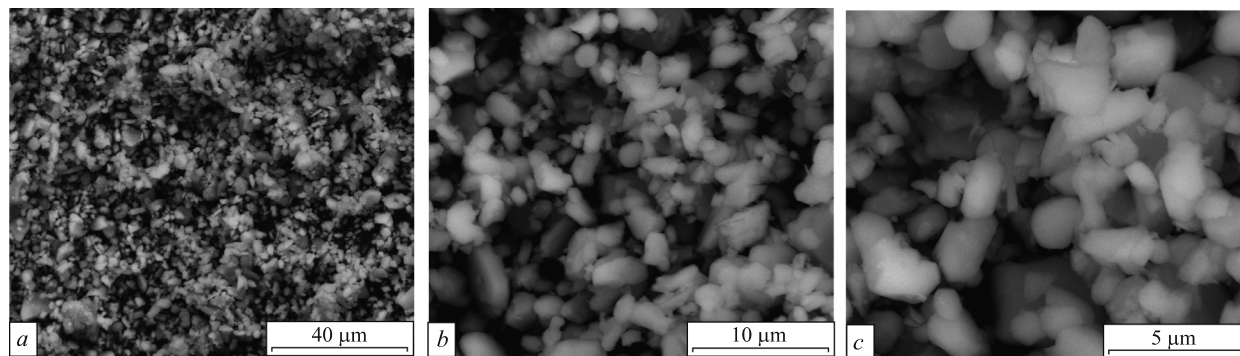


Fig. 7. SEM-picture of Nabalox NO 105 alumina ground for 14 h at different magnification.

crystallites with assize from fractions for 2–3 μm . Fine $\alpha\text{-Al}_2\text{O}_3$ particles that are finished product are plate-shaped crystallites of rounded or elongated shape.

CONCLUSION

- It has been established that during milling in a ball mill calcined Nabalox NO 105 alumina with prescribed production parameters the reduction in median particle size D_{50} is by almost a factor of 25. In the initial milling stages a coarse grain-spherulite crushing mechanism predominates. After 2–3 h the milling process is transferred into a wear phase. In this stage a no less important role is played by the cylindrical shape of milling bodies due to which there is an increase in contact area between material particles and pebble surface.

- Particle distribution within the finished finely dispersed product is bimodal in nature that is due to the structural and morphological properties of the alumina raw material. The median diameter of particles with the prescribed experimental production parameters was 2.5–2.7 μm .

- A finely dispersed activated alumina specimen obtained has properties comparable with those of well-known commercial analogs. In addition, a disadvantage of the material obtained is a high tendency towards agglomeration and sticking of finely dispersed particles (less than 3 μm) during milling. In order to overcome these production problems within manufacturing practice it is expedient to employ additives, i.e., various types of milling intensifiers.

(To be continued)

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