

USING PRODUCTION WASTE

FINELY DISPERSED LOW-ALKALI ALUMINA FOR OBTAINING CORUNDUM REFRACTORIES AND CERAMICS

A. A. Khanamirova, B. V. Nikogosyan,
B. N. Simonyan, N. I. Ingul,
L. P. Apresyan, É. V. Degtyareva,
I. L. Boyarina, and L. V. Miroshnik

UDC 666.762.11.022

The production of high-grade corundum refractories and ceramics requires the use of low-alkali alumina since the presence of alkaline metal impurities reduces the slag resistance, and impairs the mechanical and dielectric properties of the ceramics [1-4]. To improve the properties of corundum ceramics and refractories, and also platelike corundum, the presence in the low-alkali alumina of 0.10-0.15% MgO is important [1, 5-7]. The amount of industrial grade, low-alkali alumina (GN-1) delivered by the Ministry of Nonferrous Metals of the USSR (Mintsvet) to the refractories industry is very limited; the amount includes that containing MgO additions (GLMK). Therefore at the present time alumina for high-grade corundum articles is practically totally prepared directly in refractory factories by mixing alumina containing 20-50% α -Al₂O₃ with magnesium chloride, and then processing it by calcination at 1500-1550°C [8].

This alumina, like all industrial grades of low-alkali alumina for preparing both corundum articles (briquet) and ceramics, requires fine milling to a grain size of less than 10 μ m since the unmilled alumina sinters inadequately. The milling is very laborious and energy-consuming.

The Institute of General and Inorganic Chemistry in Armenia on the base of industrial waste products (anode slurries) has developed a method for obtaining finely dispersed, high quality, low-alkali alumina modified with magnesia which, according to data from KhADI and the Ukrainian Scientific-Research Institute of Refractories, sinters rapidly without milling.

In factories producing aluminum foil for anodes used in electrolytic condensers, used in modern transistor systems, they have obtained an artificial increase in the "effective" surface of the foil in order to increase the capacitance and to facilitate miniaturization of the capacitors. The artificial increase in the surface area of the foil is accomplished by the method of electrochemical processing of the material in solutions (etching), containing 1.5-30% NaCl and 0.5-7% Na₂SO₄ [9-11], at 45-92°C for 3.5-4 min, and furthermore the anode serves as the foil whose surface is being increased. In this case each year the factories produce thousands of tons of anode slurry consisting of finely grained crystalline growths of aluminum hydroxide containing chloride and (to a much less degree) sulfate of sodium. The slurry is dumped and contaminates the environment.

The specific features of the anode slurry (anode aluminum oxide insulated from the surface of the metal) are that, according to modern ideas, it is a colloidal-polymer, a discrete compound, consisting of separate particles with cross sections within the range of the colloidal degree of dispersion (10^{-5} - 10^{-7} cm) [12], in the composition and on the surface of which ions of electrolyte and water are contained [12, 13]. Furthermore, the ions of electrolyte contained in the anode aluminum oxide are subdivided into two forms [12-17]: ions that are sorbed by pores (up to 20%), held in the anode oxide by the forces of physical adsorption and removed from it during washing; and structural ions entering into the phase anode aluminum oxide by means of the substitution in its micelles of hydroxyl-ions and protons on the anions and cations of the electrolyte, being held in them on account of chemical affinity [18], and not prone to ion exchange and not removable from the anode alumina even

*Here and subsequently, mass proportions are indicated.

Institute of General and Inorganic Chemistry, Academy of Sciences of the Armenian SSR.
Kharkov Automobile-Road Institute. Ukrainian Scientific-Research Institute of Refractories.
Translated from Ogneupory, No. 10, pp. 13-17, October, 1984.

TABLE 1. Conditions for Obtaining Alumina* and Its Properties

Sample No.	Calcin. conditions		Content of R ₂ O (as Na ₂ O), %		Size of single crystals in alumina, μm
	temp., °C	time, h	in Al hydroxide	in alumina	
1	1150	2,5	0,04	0,040	0,5-2
2	1150	4,5	0,07	0,070	0,5-2
3	1100	4,0	0,04	0,028	0,5-1,5
4	1125	4,0	0,07	0,049	0,5-1,5
5	1150	4,0	0,17	0,070	0,5-2
6	1200	4,0	0,33	0,085	0,5-2

*Samples Nos. 1-4 were washed with hot distilled water with a solid: liquid ratio of 1:(5-6); samples Nos. 5 and 6 with water with a ratio of 1:(6-4).

TABLE 2. Quantity of Magnesia and Soda in the Finely Dispersed, Low-Alkali Alumina Alloyed with MgO

Content of R ₂ O (as Na ₂ O) in aluminum hydroxide, %	Content of MgO additive, %	Calcin. conditions		Content in alumina, %	
		temp., °C	time, h	MgO	Na ₂ O
0,070	0,20	1480	12	0,18	0,03
0,093	0,15	1500	10	0,11	0,06
0,043*	0,15	1480	12	0,10	0,03
0,073†	0,15‡	1500	10	0,10	0,032

*Precalcined at 1100°C for 5 h.

†Precalcined at 1300°C for 1 h.

‡1.5% H₃BO₃ also added.

TABLE 3. Chemical Composition and Density of Alumina

Alumina	Mass proportions, %								True density, g/cm ³
	Al ₂ O ₃	SiO ₂	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	Δm _{cl}	
GLMK	>99,66	0,04	<0,01	<0,016	0,017	0,23	0,035	0,10	3,95
K	>99,72	0,03	<0,01	0,030	0,040	0,16	0,010	0,10	3,97
Exptl.	>99,33	0,36*	<0,01	<0,020	0,070	0,18	0,015	0,08	3,96

*This takes into account the contamination during calcination in the furnace with silit heaters.

after careful washing. There exist experimental data [19, 20] on the preferential sorption by the anode alumina of anions, and not the cations of the electrolyte.

The specific properties and structures of anode oxides of aluminum are due to the special conditions of their formation.

Depending on the composition and concentration of the electrolyte, additives, temperature, and duration of anodic oxidation of aluminum, and subsequent processing of the pulp of anode slurry, it may have a variable composition, but it has been noted [21] that in neutral solutions of chlorides during the electrolytic treatment of aluminum, bayerite is most frequently formed.

A comparison of the peculiarities of the structure and influence of various factors on the structuring of anode alumina and ordinary gels showed that they have the same colloidal nature [22]. The mechanism of the formation of modification structures in the anode alumina during electrolysis at 20-95°C (amorphous alumina → crystalline oxide → crystalline hydroxide) is identical to the mechanism forming particles in many colloidal systems [23] and the

TABLE 4. Grain-Size Composition and Specific Surface of Alumina

Alumina	Content, %, of fractions, μm					True density, g/cm^3
	60-40	40-20	20-10	10-5	<5	
GLMK	30,8	36,4	12,8	4,0	16,0	3267
K . . .	34,6	28,3	7,7	9,2	20,0	2378
Exptl. .	3,6	6,9	6,3	25,8	57,4	7560

TABLE 5. Results of Sintering Alumina at Different Temperatures in 6 h

Alumina *	Properties of alumina, † sintered at temp., °C					
	1580		1650		1750-1780	
	P_{op} , %	ρ_{app} g/cm^3	P_{op} , %	ρ_{app} g/cm^3	P_{op} , %	ρ_{app} g/cm^3
GLMK	50,8	1,94	Not detd.		23,2-30,2	2,97-3,04
GLMK (45)	Not detd.		25,7	2,95	1,27	3,86
K (15)	27,7	2,88	18,9	3,21	0,08	3,80
Exptl.	36,0	2,53	Not detd.		2,5	3,68

*The duration of vibromilling of the alumina is indicated in parentheses, in min.

† P_{op} - open porosity; ρ_{app} - apparent density.

colloidal-disperse minerals in the weathering crust [24], but sharply different from the mechanism forming aluminio-oxide compounds during the decomposition of alkaline aluminate solutions by decomposition or carbonization [25-27] (amorphous hydroxide of aluminum \rightarrow bohmite \rightarrow bayerite \rightarrow hydrargillite).

Thus, the anode slurries differ from technical aluminum hydroxide through composition and physicochemical properties; they have an undoubted advantage over technical aluminum hydroxide during processing into nonmetallurgical alumina. These advantages are due to two of the most typical properties of anode slurries: high dispersion of the particles (0.5-6 μm against 20-300 μm for technical alumina) and the presence of alkali impurity in almost completely washable form (the content of washable R_2O in technical aluminum hydroxide is 20-50% of the total of R_2O).

The production of technical alumina with a high purity and fineness and large amounts of $\alpha\text{-Al}_2\text{O}_3$ is a complex technical problem, since with a rise in the alumina of the $\alpha\text{-Al}_2\text{O}_3$ concentration there is an increase in its hardness and abrasiveness, which significantly hinders the milling of the alumina. Using existing methods for obtaining low-alkali technical alumina, the aluminum hydroxide is calcined and the resulting alumina is treated with a diluted solution of sulfuric acid to remove impurities, after which it is calcined at 1200-1300°C in the presence of a fluorine mineralizing additive [28, 29].

To utilize the anode slurries it is necessary to use a simple method which should contribute to the maximum possible removal of washable impurities, the preservation or reduction in the fineness of the particles, and calcination in rationally selected conditions in order to obtain low-alkali, finely dispersed alumina.

The study of the anode slurries from five factories in the country producing capacitor foil showed that the slurries differ in concentrations of impurities, the size of the monocrystals (from 0.5-5.2 to 1.0-6.4 μm), phase composition (bayerite, bayerite + hydrargillite, amorphous hydroxide of alumina + bayerite, bohmite + bayerite). Many years' practice and the combined work of the Institute of General and Inorganic Chemistry of the Academy of Science Arm. SSR with the foil department of the Kanakersk aluminum factory (KANAZ) showed that the process of electrolytic treatment of aluminum foil in all capacitor factories can be carried out taking into account further utilization of the resulting waste products in conditions contributing not only to an increase in the effective surface area of the foil but also to the minimum (as at KANAZ) contamination of anode slurries with impurities of silica, iron oxide, calcium oxide, and metallic aluminum.

The method of treating the anode slurries with the production of low-alkali finely dispersed aluminum hydroxide [30] is as follows: the slurry [6.5-10% R_2O (as Na_2O), 0.03-0.07%

SiO_2 , 0.003-0.010% Fe_2O_3]* is washed with hot (70-80°C) distilled water with a solid-liquid ratio of 1:(5-6) to a residual concentration of R_2O (as Na_2O) equal to 0.17-0.35%, washed with 0.4-0.9% solution of NH_4Cl with a solid-liquid ratio of 1:(1.5-2), heated at 70-80°C for 5-10 min, filtered, and washed with hot water until the disappearance of the chlorine in the wash liquids. This treatment ensures a reduction in the content of alkali in the resulting aluminum hydroxide of up to 0.05-0.07% R_2O (as Na_2O) and a reduction in the size of the single crystals from 0.5-5.2 to 0.5-2 μm .

Studies were made of the process of thermal decomposition (calcination) of the finely dispersed aluminum hydroxide, both without mineralizing additives (samples Nos. 1 and 2) and in the presence of 0.4% aluminum fluoride (Nos. 3-6%) and also the crystallization from them of alumina (Table 1). The aluminum hydroxide was obtained from anode slurries. It was found that the low-alkali finely dispersed alumina containing 98-100% $\alpha\text{-Al}_2\text{O}_3$ with a density of 3.98-4.00 g/cm^3 and a specific surface of about 1 m^2/g can be obtained during the calcination of finely dispersed aluminum hydroxide both without mineralizers and in the presence of AlF_3 .

According to the microstructure, grain, phase, and chemical compositions of samples Nos. 1 and 2, obtained without mineralizers, and alumina samples No. 5 and No. 6, they are similar to low-alkali alumina grade GN-1. Alumina of samples Nos. 3 and 4 obtained in the presence of fluoride mineralizer, according to the microstructure and phase composition, is also similar to alumina grade GN-1, but in terms of purity and dispersion it surpasses both alumina GN-1 and also alumina A-14 produced by the Alcoa Company and PV 1179 and PV 1269 produced by Smiths Industries Ltd. (USA).

To obtain low-alkali alumina containing MgO , the finely dispersed aluminum hydroxide is mixed with 0.15-0.2% MgO (in the form of a solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and, after drying, is calcined at 1480°C for 12 h, or at 1500°C for 10 h.

It is also possible to obtain low-alkali alumina by precalcination of the hydroxide at 1100°C in 5 h, or at 1300°C for 1 h, by adding to the weakly calcined alumina 0.15% MgO (as a solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and calcination after drying at 1480°C for 12 h or at 1500°C for 10 h. All the methods used ensure similar contents in the alumina of magnesium and sodium oxides (Table 2).

The study of the average samples of experimental alumina obtained by the Institute was done with industrial alumina GLMK and alumina K prepared for the production of "Kador" ceramic; this showed that all types of alumina are close in chemical composition, the content of $\alpha\text{-Al}_2\text{O}_3$, and density, but significantly different in terms of microstructure and grain-size composition (Tables 3 and 4).

The content of $\alpha\text{-Al}_2\text{O}_3$ in the GLMK alumina is 94-96%, and in the alumina grade K and experimental product - 97-98%. The quantity of grains measuring less than 10 μm , determining their sintering in the experimental alumina, is substantially higher (2.8-4.2 times) than in the GLMK alumina and K alumina, which confers a greater (2-3 times) surface area. Thus, the experimental alumina does not require grinding in refractories factories when it is used as a raw material for making corundum refractories and ceramics, while the GLMK and K varieties need milling during which the Al_2O_3 content is reduced to 99.45-99.49% (on account of the iron pickup).

A study of the sintering of three types of alumina showed that GLMK and K without pre-milling do not sinter up to temperatures of 1750-1780°C, while the experimental alumina sinters very rapidly (Table 5).

Corundum ceramic is used as blanks for growing single crystals of leucosapphires [31] and so articles made of the experimental alumina were tested for this purpose. Tests showed that high-grade single crystals could be grown from this material without boiling.

Thus, the results indicate that finely dispersed low-alkali alumina obtained from waste (anode slurry) is suitable for making articles to produce single crystals, and also is very promising for the production of platelike corundum chamotte, various corundum articles and transparent ceramics. The exclusion of milling the alumina and its deep purification ensures a reduction in energy use in the production of corundum refractories and ceramics, which yields a big saving.

*Content of impurities in the anode slurry and aluminum hydroxide is indicated, after recalculation, as Al_2O_3 .

CONCLUSIONS

Using low-alkali, finely dispersed aluminum hydroxide, separated from anode slurries, we obtained low-alkali, deeply calcined alumina in a single stage without mineralizing additives and also in the presence of small amounts of aluminum fluoride with an addition of magnesium chloride at lower temperatures than with the industrial technology. The low cost of the alumina obtained from this source and their wastes, which are dumped, the accomplishment of a single-stage calcination instead of the double-stage calcination of aluminum hydroxide, using intermediate washing with a solution of sulfuric acid, the exclusion of expensive labor- and energy-consuming operations of milling the alumina and cleaning it to remove iron impurity all contribute to a marked cheapening and a simplification of the production method for deeply calcined, low-alkali alumina.

The resulting low-alkali alumina, alloyed with magnesia, has a high dispersion and does not require premilling for the production of articles for growing single crystals of leucosapphire, corundum refractories and ceramics, since the degree of its sintering is equal to that of industrial alumina after milling.

We recommend the production of large batches of low-alkali, finely dispersed alumina by the method developed by the Institute. The method may be used for the production of high-duty corundum refractories and ceramics.

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CALCULATING THERMOELASTIC STRESSES IN A HOLLOW CERAMIC
CYLINDER WITH A LINEAR THERMAL LOADING SCHEDULE

M. I. Landa, N. N. Kopytov,
and N. M. Tsirel'man

UDC 666.762.11.017:539.4.014.11

At the present time, when the advantages of heat-resistant and refractory materials based on metals and used in aircraft components and other thermally and mechanically loaded design parts are already largely exhausted, the attention of designers, technologists, and material scientists is turning to composites and ceramics.

However, such materials are brittle, have poor heat conductivity, and inadequate thermal-shock resistance, especially in the temperature range preceding their plastic deformation. This makes it necessary to produce a precise determination of the thermoelastic stresses and temperature fields in elements of actual constructions. In this article these characteristics are studied analytically and compared with experimental results for the distribution of temperature during the determination of the thermal-shock resistance of ceramic hollow cylinders.

The authors obtained a decision in the electronic computer for the corresponding non-linear edge problem of thermal conductivity. In this case, a study was made of the temperature relationships for the thermophysical properties of the materials and the degree of blackness of their surfaces; and in limiting conditions on the external surface account was taken of the heat exchange with the surroundings according to the law of free convection and radiation, when on the internal surface of the cylinder the temperature increased with time according to the linear rule.

The temperature fields obtained in the computer were used to determine the thermoelastic stresses in the hollow cylinder assuming a quasistationary state at the moment of time being considered from the start of the thermal loading.

The solution of the edge problem for thermal conductivity includes:

- 1) the equation for the spread of heat in the hollow cylinder:

$$\bar{c}_Q(\Theta) \frac{\partial \Theta}{\partial Fo} = \frac{1}{\eta} \cdot \frac{\partial}{\partial \eta} \left[\bar{\lambda}(\Theta) \eta \frac{\partial \Theta}{\partial \eta} \right], \quad (1)$$

$$1 < \eta < 1 + \Delta, Fo > 0;$$

- 2) the simplest initial condition:

$$\Theta(Fo=0, \eta) = 1; \quad (2)$$

- 3) the limiting condition corresponding to the linear temperature rise with time on the internal surface of the cylinder:

$$\Theta(Fo, \eta=1) = 1 + \gamma Fo; \quad (3)$$

- 4) the boundary condition corresponding to the removal of heat from the external surface of the cylinder according to the radiation-convection law:

$$-\bar{\lambda}(\Theta) \frac{\partial \Theta}{\partial \eta} \Big|_{\eta=1+\Delta} = Sk[\Theta^4(1+\Delta, Fo) - 1] + \chi[\Theta(1+\Delta, Fo) - 1]^{1.25}. \quad (4)$$

S. Ufimsk Ordzhonikidze Aviation Institute. Translated from *Ogneupory*, No. 10, pp. 18-21, October, 1984.