

Synthesis of high-purity α -Al₂O₃ from boehmite by high temperature vacuum treatment

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In this study a simple and environmentally benign method for conversion of technical purity Al into high-purity alumina is described. The method is based on hydrothermal oxidation of aluminium and subsequent high temperature purification of aluminium oxide. Deep purification is achieved by high-temperature vacuum treatment of aluminium oxide at temperature of 1600–1750 °C. Structure and chemical composition of reaction products obtained at experimental conditions at different steps of method are examined in presented work. It has been shown that by proposed method the Al powder of technical purity (99.8 wt.%) can be converted into high-purity alumina (99.997 wt.%). Molecular mechanics simulation of impurities segregation to the (0001) surface of alumina crystal has been carried out. The simulation revealed a correlation between the strength of segregation and the efficiency of impurities removal from alumina during high-temperature vacuum treatment.

Key words: Alumina, High purity, Hydrothermal oxidation, Boehmite, Vacuum heat treatment.

Introduction

The lack of economically efficient and environmentally benign methods for high-purity alumina production hampers technological development of optical and semiconductor industry, quantum electronics, electric-power industry, instrument engineering, etc. High-purity alumina is applied for the manufacture of high-quality optics, monocrystal yttrium-aluminium garnets and leucosapphires. Leucosapphires are widely used for a number of applications such as production of LEDs, substrates for integral microchips, laser diodes, implants, artificial joints, microscalpels, etc. High-purity aluminium oxide is also used for the production of refractory shapes for manufacture of ultra-pure products. Porous and ultra-pure alumina appears to be generally utilized to the manufacture of catalysts and adsorbents. According to [1] about 40 percent of world high-purity alumina production is covered by Sumitomo Corporation in Japan, and just over half of alumina demands is provided by several Chinese companies.

Hydrolysis of aluminium isopropylate [2, 3], thermal decomposition of aluminium isopropoxide [4], and thermal decomposition of aluminium nitrate [5] are used for high-purity alumina manufacturing. Among them, the alcoholate method of aluminium oxide production is the main method which supplies raw material for industrial leucosapphires production [6]. In this process aluminium isopropoxide is synthesized by dissolution of starting Al in isopropanol. The aluminium isopropoxide undergoes

several purification steps in order to decrease impurity level and then it is hydrolysed by liquid water or water steam. During the mentioned process aluminium hydroxide is formed. Further it undergoes calcination to produce alumina. Alcoholate method utilizes aggressive chemicals which cause dangerous pollution.

Hydrothermal oxidation of aluminium is a promising method for the production of ultra fine aluminium oxides and hydroxides [7]. It has been found previously that it is possible to produce boehmite (aluminium oxyhydroxide) with large surface area and microporous structure in a continuous hydrothermal reactor at temperature of approximately 300 °C and pressure of about 10 MPa without of any additives [8]. At hydrothermal oxidation the aluminium with technical purity (99.8 wt.%) in the form of micron-sized powder and distilled water were only used as the initial reagents. Al conversion level was close to 100% [9, 10].

In this study a simple and environmentally benign method for conversion of Al of technical purity into high-purity alumina is presented. The method is based on hydrothermal oxidation of aluminum and subsequent high temperature purification of solid oxidation product. Structure and chemical composition of products obtained at different temperatures and exposure times are investigated and systematized. An atomistic simulation of impurities segregation to the surface of alumina crystal has been carried out. Simulation results have been compared with the experimental data.

Experimental

Description of high-purity α -Al₂O₃ production technology

The method of high-purity α -Al₂O₃ production

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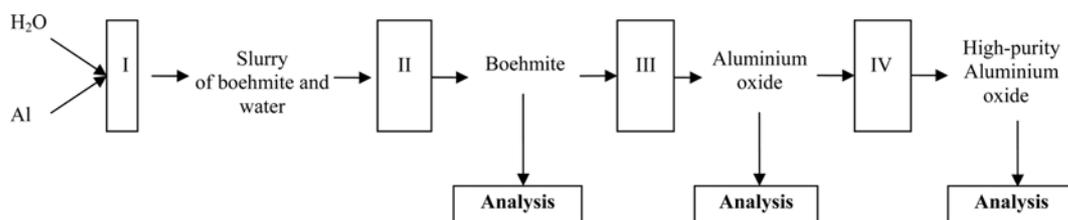


Fig. 1. The production method of high-purity aluminium oxide. I: hydrothermal oxidation of aluminium (boehmite synthesis), II: boehmite and water separation, III: removal of water from the boehmite crystal lattice by calcination in muffle furnace (aluminium oxide production), and IV: high temperature purification.

consisted of 4 main steps (see Fig. 1) [11]. The first step is boehmite formation at temperature of about 300 °C and pressure of about 10 MPa. Boehmite (γ - AlOOH) is formed in accordance with the following reaction:



At the second step, dry boehmite is obtained by decanting and drying of boehmite-water slurry.

At the third step, the boehmite is placed into the muffle furnace and heated in order to remove the crystallized water. During the heating the boehmite transforms into γ - Al_2O_3 or α - Al_2O_3 depending on temperature:



At the final step, the aluminium oxide obtained by calcination in muffle furnace is placed into the vacuum furnace to provide high-temperature purification. During this process the end product (α - Al_2O_3) is formed:



A vacuum drying oven VD-53 (Binder GmbH) was used to dry boehmite slurry and remove non-bounded water. To remove water from the boehmite crystal lattice and to transform it into aluminium oxide a muffle furnace LHT 08/16 (Nabertherm) was used. High temperature vacuum purification of aluminium oxide was carried out in a vacuum furnace SNV-1.3.1/20 (VNIIEITO).

At every step, reaction products were examined by scanning electron microscopy (SEM), X-ray diffractometry (XRD), adsorption analysis and mass spectrometric analysis (chemistry analysis).

Methods for samples examination

The morphology of the surface of boehmite and products of its calcination were examined on a scanning electron microscope (Jeol JSM-7401F). A carbon base was used to place the samples in the field of view of

microscope.

The phase composition of boehmite and aluminium oxide samples was examined by XRD on a diffractometer Thermo ARL XTRA applying $\text{CuK}\alpha$ emission ($\lambda = 0.15418$ nm). X-ray diffraction patterns were recorded within the angle of $2\theta = 10$ -100 degrees with angle step of 0.75 degrees/min.

The specific surface areas of the boehmite and aluminium oxide samples were defined by low-temperature nitrogen adsorption. The nitrogen adsorption isotherm was plotted using four data points. The specific surface area was derived from the adsorption isotherm using Bruner-Emmett-Teller equations (BET) [12].

To study the chemical composition of boehmite and aluminium oxide samples inductively coupled plasma mass spectrometer ICP-MS, X-2 (Thermo Scientific, USA) was used. Before mass-spectrographic analysis, the sample was dissolved in the acid or mixture of acids in open systems or in an autoclave. The solution contained no more than 0.05-0.2 percent of the sample material. Further the solution was atomized by argon flow and introduced into plasma in the form of fine aerosol. When aerosol particles passed through the plasma (during approximately 2 ms) the processes of aerosol desolvation, evaporation of solid particles, atomization, excitation and ionization of atoms, took place. From plasma region the ions were directed through special interface into the vacuum part of the mass-spectrometer, in which the formation of positive ion beam with the simultaneous photon and neutral particle blocking took place. Then ions entered into a quadrupole mass analyser, where separation of particles according to mass-to-charge ratio occurred. The intensity of ions flux with the same mass-to-charge ratio was measured by a detecting system and the obtained mass-spectrums were stored in computer database. An essential disadvantage of applied method in respect to aluminium based materials was the impossibility to define the silicon content since silicon acids were used as solvents.

To provide the transformation of boehmite into alumina the 100-ml alumina crucible was used. Crucible with the sample was installed in a central zone of the muffle furnace LHT 08/16. The muffle furnace chamber dimensions were $150 \times 300 \times 150$ mm. The furnace was equipped with molybdenum disilicide open heaters. Heat

insulation of furnace was made of alumina.

Final purification process was carried out during heating the product in the vacuum high temperature furnace SNV 1.3.1/20. Thermal chamber has dimensions $100 \times 300 \times 100$ mm. The heaters of the furnace were made of tungsten, the heat protection shields were made of molybdenum. The crucible with aluminium oxide was placed into the isothermal central part of the chamber. Crucibles were made of tungsten or molybdenum. Crucibles internal volume was about 100 ml (80 mm diameter, 40 mm height, 5 mm wall thickness). For temperature measurements two tungsten-rhenium thermocouples were used. The hot junction of the first thermocouple was at the centre of the thermal chamber about 2 cm above the top of the crucible. The heating control system operates in accordance with the signal of the first thermocouple. The hot junction of the second thermocouple was covered with the cap made of polycrystal alumina which was dipped into the sample in crucible. At temperature level more than 1000°C the readings of two thermocouples did not differ more than 10 degrees. At temperatures between 1600°C and 1750°C the difference between thermocouples readings lied in the range of $5\text{--}7^\circ\text{C}$.

Starting materials

Aluminium powder of technical purity (produced by SUAL-PM Company, Russia) and distilled water were used as starting materials in hydrothermal oxidation step. Fig. 2 and Fig. 3 show the particle size distribution of SEM image of aluminium powders, respectively, illustrating that starting aluminium powder mainly contains spherical particles with diameters up to $60\ \mu\text{m}$ and average diameter of about $20\ \mu\text{m}$.

Specific area of Al powder was calculated from particle size distribution curves (Fig. 2) to be of $\sim 0.1\ \text{m}^2/\text{g}$.

In Table 1 the results of mass spectrometric analysis of aluminium powder composition are shown. Total

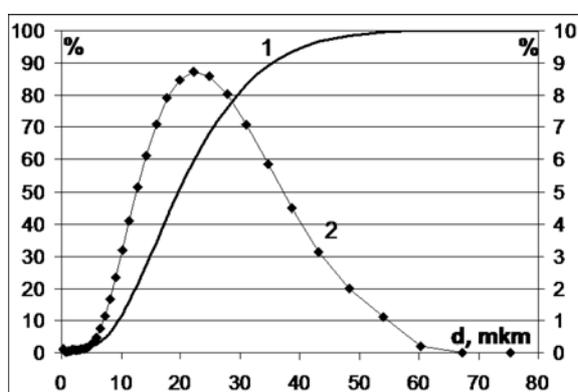


Fig. 2. Particle size distribution of starting aluminium powders used for boehmite production. 1: cumulative particle size distribution, 2: differential particle size distribution, and d: particle diameters.

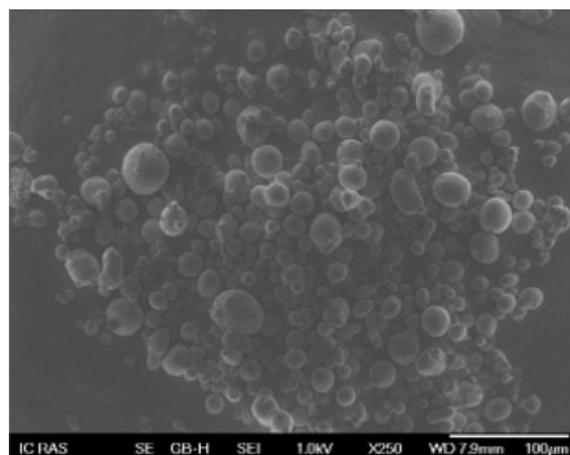


Fig. 3. SEM image of starting aluminium powder.

Table 1. -Chemical composition of starting aluminium. DL (the detection limit for the element for the analytical procedure employed).

Element	DL, ppm	Aluminium powder
Na	25	< DL
Mg	2	12.5
Al		Base
K	9	< DL
Ca	6	< DL
Ti	1.1	6.9
V	0.4	55.8
Cr	0.4	27.2
Mn	0.3	23.2
Fe	2	1057
Co	0.0	1.6
Ni	0.4	54.1
Cu	0.3	5.5
Zn	0.3	83.3
Ga	0.03	82.4
Mo	0.02	2.6
W	0.07	0.22
Sum, ppm		1452

content of all impurities in the powder was equal to 1452 ppm (not including silicon impurity). Major part of impurities is represented by iron (more than 1000 ppm). According to well-known literature data, the content of silicon in aluminium powders of technical purity varies from 300 to 700 ppm. The results of chemical analysis are in agreement with the data of a conformity certificate for powder (more than 99.8 wt.%, less than 2000 ppm).

Results and Discussion

Structural properties of boehmite and products of its heat treatment

Properties of boehmite

Boehmite is formed in reactor for hydrothermal oxidation of aluminium according to reaction (1). The XRD analysis of solid product of aluminium hydrothermal oxidation affirmed that its main phase is crystalline γ - $AlOOH$ (all diffraction peaks in XRD pattern corresponded to γ - $AlOOH$ [8]). From X-ray peak broadening it was evaluated that the average size of crystallites is about 30-60 nm.

The solid boehmite formed by the hydrothermal oxidation of aluminium had a specific surface area of $83 \text{ m}^2/\text{g}$ (obtained by BET analysis).

SEM images (Figs. 3 and 4) show that particles are significantly smaller than starting Al particles. It can also be seen that boehmite particles consist of agglomerates with sizes of about several micrometers. Agglomerates consist of nanocrystals with sizes from 10 to 200 nanometres. Nanoscale boehmite structure as well as the proposed phenomenon of segregation of impurity atoms on the surface of crystals is expected to assist the effective impurities removal from crystal lattice during subsequent heat treatment at the next stages of thermal processing.

Properties of aluminium oxide obtained by calcination in muffle furnace

The boehmite was heated in muffle furnace at different

Table 2. The change of specific surface area from boehmite to aluminium oxide.

Sample	Synthesis temperature	Specific surface area
Boehmite	300 °C	$83 \text{ m}^2/\text{g}$
Aluminium oxide	600 °C	$98 \text{ m}^2/\text{g}$
Aluminium oxide	1100 °C	$14 \text{ m}^2/\text{g}$
Aluminium oxide	1300 °C	$8 \text{ m}^2/\text{g}$

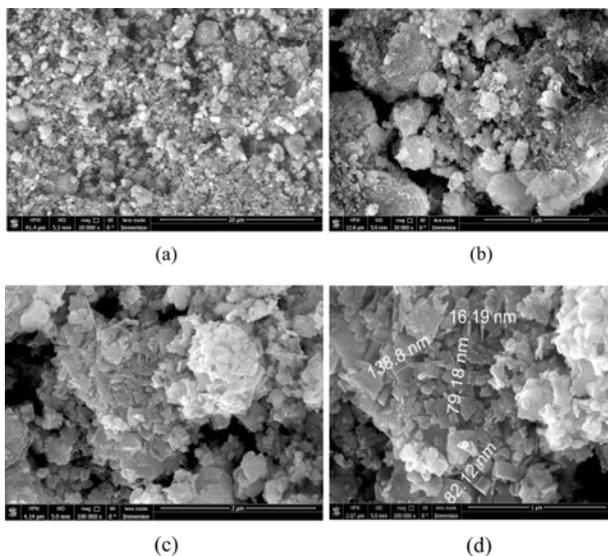


Fig. 4. SEM images of boehmite (resolution: (a) 20 μm , (b) 5 μm , (c) 2 μm , (d) 1 μm).

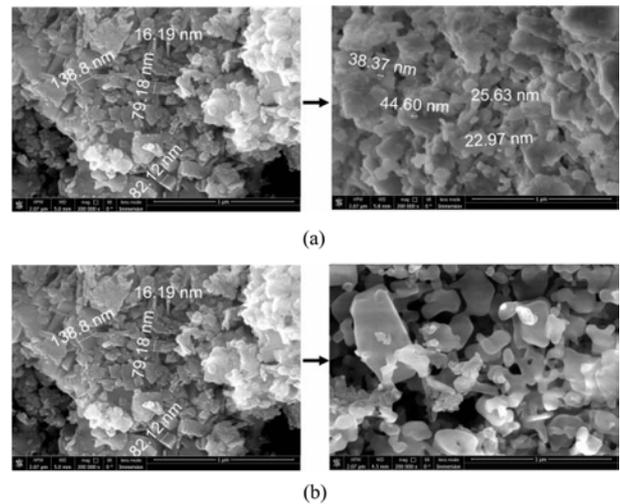


Fig. 5. Changes in the boehmite structure after calcination at (a) 600 °C and (b) 1100 °C. (scale: 1 μm) The left images are the images of the boehmite and the right images are the images of the aluminium oxide.

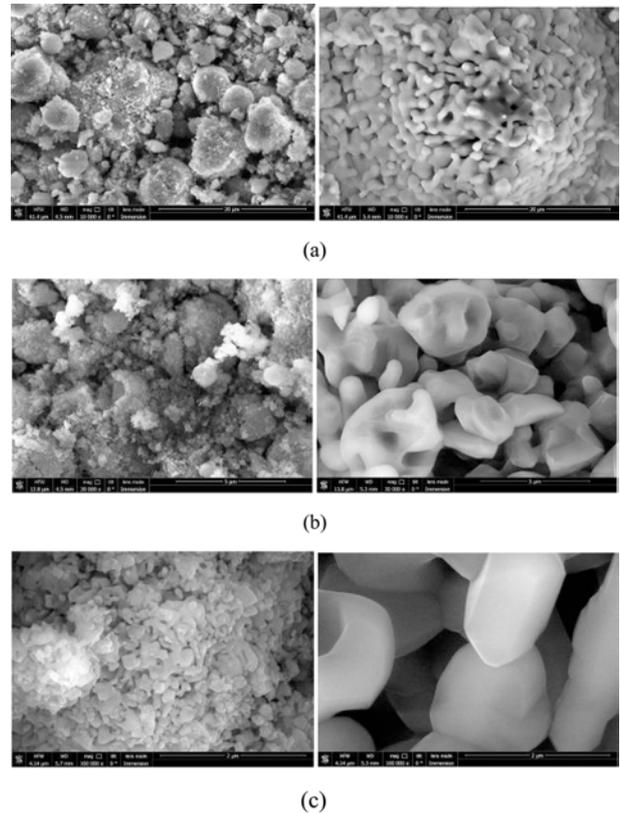


Fig. 6. Al_2O_3 obtained after boehmite treatment in the muffle furnace at temperature of 1100 °C (left images) and α - Al_2O_3 after heat treatment in the vacuum furnace at 1750 °C (right images). Image scales: (a) 20 μm , (b) 5 μm , (c) 2 μm .

temperatures. The aim of this stage of treatment was to remove the crystallized water and to transform $AlOOH$ into aluminium oxide. After transformation the mass of the sample decreased by 14.86 percent. The structure of aluminium oxide obtained in the muffle furnace depended on the maximum temperature. After heating

up to 600 °C aluminium oxide with specific surface area of 98 m²/g was formed. Therefore, the specific surface area slightly increased in comparison with those for boehmite. After heating up to 1100 °C the aluminium oxide with specific surface area of 14 m²/g was formed. After heating up to 1300 °C the specific surface area decreased to 8 m²/g. The change of specific surface area from boehmite to aluminium oxide is shown in Table 2.

In Fig. 5 oxide structure after heating up to 600 °C (Fig. 5(a)) and 1100 °C (Fig. 5(b)) is shown. At 600 °C γ -Al₂O₃ is formed and porous structure of the material remains practically unaffected. At 1100 °C oxide crystals undergo sintering and form particles of larger size. Therefore, SEM examination results are in accordance with specific surface area measurements.

Properties of aluminium oxide after high temperature treatment in vacuum

Powder samples of aluminium oxide were heated in vacuum furnace at different temperatures in the range of 1600-1750 °C. According to the results of XRD analysis, all the samples obtained at these temperatures consisted of 100% α -Al₂O₃. In Fig. 6 SEM images of aluminium oxide particles obtained in the muffle furnace at temperature of 1100 °C and α -Al₂O₃ particles obtained after heat treatment in the vacuum furnace at temperature of 1750 °C are shown. The images show the change of particle sizes of the oxide after its heating to temperature of 1750 °C. It is seen

that the sintering of the separate small crystals occurs. It leads to formation of larger particles after exposure of Al₂O₃ powder at high temperature. Typical sizes of the crystals increase up to several microns. The bulk density of the powder increases by ~0.3 g/cm³ up to approximately 1.4 g/cm³.

Chemical composition of boehmite and products of its heat treatment

Chemical composition of boehmite and aluminium oxide obtained by calcination in muffle furnace

The first set of the experiments in muffle furnace was carried out to define if it was possible to remove impurities from the samples by heating in air at moderate temperatures. Heating was carried out up to 1100, 1300, and 1500 °C. Exposure time at these temperatures was usually the same-equal to 2 hrs. At temperature of 1500 °C an extra experiment with the exposure time increased up to 5 hrs was carried out. Heating was carried out in an alumina crucible in air. The results of the chemical analysis of the boehmite and the aluminium oxide synthesized from it in muffle furnace in air atmosphere are presented in Table 3.

The results of the chemical analysis of the boehmite show a two-fold decrease of the impurity concentration relative to the starting Al (see Tab. 1). It may be explained taking into account equation (1). Oxidation of 1 g of Al leads to formation of 2.22 g of boehmite. It is assumed that water is clean enough. Then, impurities contained in the starting Al are distributing inside the

Table 3. Chemical analysis results. A: boehmite, B1, B2, B3: Al₂O₃ obtained at temperatures of 1100, 1300 and 1500 °C with exposure time of 2 hrs, B4 - Al₂O₃ obtained at 1500 °C and exposure time of 5 hours (DL: the detection limit for the element).

Element	DL, ppm	Aluminum powder (as listed in Table 1)	A	B1	B2	B3	B4
Na	0.9	< 25	1.4	5.5	13.2	46.8	48.7
Mg	0.3	12.5	3.5	3.8	4.0	3.9	4.3
Al		Base	Base	Base	Base	Base	Base
K	1	< 9	< DL	2.5	2.0	7.9	10.0
Ca	1	< 6	< DL				
Ti	0.6	6.9	2.8	3.5	3.8	4.4	7.4
V	0.2	55.8	28.4	31.5	33.8	33.1	33.1
Cr	0.4	27.2	22.0	24.3	26.7	26.4	27.4
Mn	0.2	23.2	10.8	12.4	13.2	13.4	12.0
Fe	0.8	1057	317	364	385	372	395
Co	0.02	1.6	0.76	0.83	0.89	0.81	0.78
Ni	0.5	54.1	21.8	24.8	26.5	25.3	25.7
Cu	0.4	5.5	1.6	1.9	1.9	0.64	0.52
Zn	0.1	83.3	27.9	31.8	33.7	12.0	11.8
Ga	0.2	82.4	34.9	39.9	42.6	43.0	42.9
Mo	0.1	2.6	1.2	3.8	1.9	9.2	14.3
W	0.09	0.22	0.31	0.39	0.30	0.56	0.61
Sum, ppm		1452	476.2	552.1	590.8	600.5	635.4

boehmite crystal lattice, and their specific content decreases. Boehmite purification is also assisted by decantation of the boehmite-water slurry produced in the reactor. Some part of the impurities is dissolved in water and it goes away with draining water.

After heat processing in the muffle furnace, the purity of samples become approximately 15% lower (Table 3, columns A&B1). It can be explained by the decrease of the sample mass during hydroxide-oxide transformation, since the molecular weight of Al_2O_3 is 14.86 percent less than that of AlOOH .

Chemical composition data show increase of impurities content with growth of temperature or exposure time. It is most likely caused by contamination of the samples by the impurities sublimated from the surfaces of the furnace insulation and the surfaces of the heaters made of molybdenum disilicide. The content of Na, K, Ti, Mo significantly increases with growth of processing temperature and exposure time at 1500 °C. Well-defined decrease takes place only for the impurities of Cu and Zn in the samples obtained at 1500 °C.

Experiments indicated that after processing in the muffle furnace aluminium oxide was not purified. Contrarily with increase of the processing temperature obtained aluminium oxide became dirtier. Nevertheless dehydration in the muffle furnace is an important stage. Boehmite dehydration begins after 40 °C. At these temperatures tungsten from which the vacuum furnace heaters are manufactured may be seriously damaged at oxidizing by released water steam.

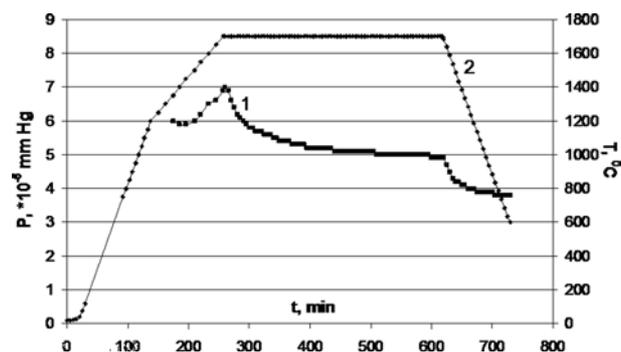


Fig. 7. Temperature and pressure records in the experiment with maximum temperature of 1700 °C and exposure time of 6 hrs (1: pressure and 2: temperature).

Chemical composition of aluminium oxide after high temperature treatment in vacuum

The aim of high temperature treatment in vacuum was the investigation of the influences of maximum treatment temperature (from 1600 to 1750 °C) on chemical composition of Al_2O_3 . The heating rate was the same for all the experiments. Fig. 7 shows an example thermogram and a pressure record. The vacuum level in the furnace was measured by ionization pressure gauge. In each experiment the pressure within the thermal chamber did not exceed 10^{-4} torr. Pressure increasing when temperature approaches the maximum value (see Fig. 7) is usual phenomena. It explained by sublimation from the surfaces of the heaters and chamber construction elements.

In high temperature experiments aluminium oxide

Table 4. Chemical compositions of aluminium oxide after heat treatment in muffle furnace at (C1) 1600 °C-6 hrs, (2) 1700 °C-1 hr, (C3) 1700 °C-6 hrs, and (C4) 1750 °C-2 hrs. Samples C1-C3 were obtained in tungsten crucible, sample C4 was obtained in molybdenum crucible. DL (the detection limit for the element).

Element	DL, ppm	B	C1	C2	C3	C4
Na	2	< DL	4.8	< DL	< DL	< DL
Mg	1	9.2	8.1	8.1	10.1	1.3
Al		Base	Base	Base	Base	Base
K	2	< DL	< DL	< DL	< DL	< DL
Ca	2	< DL	< DL	< DL	< DL	< DL
Ti	1	3.7	3.8	4.1	4.1	< DL
V	0.1	4.9	4.9	4.9	5.2	8.5
Cr	1	9.3	9.2	9.4	10.3	4.9
Mn	0.2	10.4	2.9	2.8	0.6	< DL
Fe	3	437	203	190	109	10.2
Co	0.1	0.21	< DL	< DL	< DL	< DL
Ni	0.1	5.5	2.4	2	1.99	< DL
Cu	3	< DL	< DL	< DL	< DL	< DL
Zn	0	76.8	< DL	< DL	< DL	< DL
Ga	0	30.7	8.5	6.4	3.6	0.51
Mo	0.04	0.52	< DL	< DL	< DL	1.6
W	0.07	0.13	110	220	220	6.7
Sum, ppm		588.36	358	448	364.89	33.7
Sum (without W), ppm		588.23	248	228	144.89	27

samples obtained in muffle furnace at 1100 °C were used. Comparison of sample compositions obtained in muffle furnace at 1100 °C and α -Al₂O₃ samples after high temperature experiments at different temperatures and exposure times are presented in Table 4.

The results of chemical analysis show that the content of iron in the sample obtained at 1600 °C with exposure time of 6 hours is equal to 203 ppm that is about two times more than the iron content in the sample obtained at 1700 °C with the same exposure time. The results of chemical analysis also demonstrate that at 1700 °C the increase of exposure time from 1hr to 6 hrs results in the decrease of the iron content from 190 to 109 ppm. Heating in vacuum at temperatures up to 1700 °C resulted in the decrease in the content of Fe, Mn, Co, Ni, Zn, Ga, Mo impurities. The content of Mg, Cr, Ti and V impurities was almost unaffected. The content of W impurity increased.

The increase of W impurity is probably caused by the sublimation of metal from the surface of the tungsten crucible used in these experiments. To eliminate this effect, in further experiment a molybdenum crucible was used. The results of chemical analysis of sample obtained in experiment with molybdenum crucible confirm the assumption mentioned above. The sample obtained in molybdenum crucible at 1750 °C had the tungsten content of 6.7 ppm only. We assume that sublimation of tungsten from crucible surface appears to cause the local extra partial pressure of tungsten vapour in the volume in the vicinity of aluminium oxide sample. It could lead to tungsten sedimentation on the sample surface and impede the effective purification.

In aluminium oxide sample obtained at 1750 °C and exposure of 2 hours the total content of impurities was 33.7 ppm (without accounting of Si). Without accounting W impurities, total content of other impurities was 27 ppm. By examination of this sample through laser ablation and inductively coupled plasma mass spectrometry it was established that the content of silicon does not exceed 5 ppm. Thus chemical purity of the obtained aluminium oxide powder is equal to 99.997 percent (33 ppm). This purity of aluminium oxide powder satisfies the requirements of leucosapphire manufacturers. However, the production of leucosapphire monocrystals of high quality for LED manufacturing need the raw material satisfying the minimum content requirements for each kind of impurities. In the samples produced in our experiments (see Table 4) the contents of iron and chromium are close to the permissible limit. However, the comparison of the results of chemical analysis of samples C1-C4 (see Table 4) shows that the contents of Fe and Cr can be reduced whether by increase of processing temperature or by increase of exposure time. The extra contents of iron and chromium could be also caused by the overheating of steel walls of vacuum chamber. Vacuum furnace used in experiments had been designed for operation temperatures less than

1800 °C. So the working temperatures were close to maximum admissible temperature for this furnace. Therefore further improvement of the considered technology demands the use of a furnace designed for higher operation temperatures (up to 2200 °C).

Atomistic simulation of impurity segregation at the surface of α -Al₂O₃

Details of calculation of impurity segregation free energy

For the development of theoretical bases for high-temperature purification of aluminium oxide in vacuum, the data on the chemical potential changing associated with the transfer of impurities from the crystal volume to its surface and into the gas phase are of great importance. A chemical potential profile determines the rate of impurity diffusion to surface [13] and its subsequent evaporation (sublimation) as well as the thermodynamic limit of purification for each kind of impurity.

In this study the calculation of free energy difference ΔG between the surface and the bulk states has been performed for some critical impurities such as Mg²⁺, Cr³⁺, Fe²⁺, Fe³⁺, Ti⁴⁺. The value of free energy change ΔG characterizes an element tendency to surface segregation, i.e. the tendency to concentration at crystal surface. Some early investigations of the evaporation kinetics of some volatile elements from metals demonstrated the importance of the segregation process involving the increase in impurity concentration on a free surface during the initial stage of heating the sample in vacuum and subsequent decrease in the segregated element concentration by evaporation [14].

In this work the atomistic simulation has been performed, using the technique of constructing an initial atomic configuration of a crystal and the conventional static relaxation method (molecular mechanics). To describe the ions interactions the Born model of ionic crystals has been used. The parameters of interactions have been taken from [15].

To calculate the impurity free energy difference G between the surface and the bulk states the process involving interchange of positions between an impurity cation in the α -Al₂O₃ bulk and a randomly selected Al³⁺ cation on the surface was analysed. The (0001) surface was investigated as one of the most stable low index surfaces of α -Al₂O₃. It was shown early that ΔG is negligibly affected by the entropy factor and vibrational modes [16]. So the free energy difference was defined as the difference in static configurational energies of a crystal after relaxation for two impurity locations: on the surface and in the bulk.

Analysis of correlations between theoretical and experimental data

In Table 5 there are the results of the calculation of free energy change ΔG associated with the impurity transfer from the bulk of α -Al₂O₃ crystal lattice to the

Table 5. The change in the free energy G values for bulk and surface fields for some critical impurities.

Element	Mg ²⁺	Fe ²⁺	Fe ³⁺	Cr ³⁺	Ti ⁴⁺
G , eV	-0.6	-1.2	0.3	0.2	1.4

Al₂O₃ (0001) surface. For Fe²⁺ it was rather high negative value of ΔG indicating the energetically favourable arrangement of these impurity ions on the surface. Samples of aluminium oxide obtained by calcination in the muffle furnace have high iron content (~400 ppm) and the calcination in vacuum may lead to the formation of FeO nanocrystalline phase on their surfaces due to iron segregation. The same effect has been observed previously for yttrium [17]. In experiments on evaporation of chondrites and multicomponent materials, those composition imitates the solar matter, FeO proved to be one of the most volatile and removable components at temperatures of 1500-2000 °C [1819]. That result is in good agreement with the above presented experimental data showing that the content of iron decreases by almost two orders when temperature increases from 1500 to 1750 °C.

The free energy change for Mg²⁺ ions also indicates that the segregation is thermodynamically favourable. However the change in the magnesium content in the aluminium oxide samples was not observed at temperatures of 1500-1700 °C. It correlates with lower volatility of MgO in comparison with FeO that was observed in some other studies. For example, at 1580 °C the MgO evaporation from multicomponent oxide is not observed [19], but when temperature approaches ~1800 °C evaporation rate for MgO significantly increases [18]. In this study the decrease in magnesium content at 1750 °C was also observed that demonstrates the necessity of further optimization of vacuum heating procedure.

For Cr³⁺ G has small positive value that indicates no surface segregation and corresponds to the ratio of the impurity contents at the surface and in the bulk at temperature of ~2000 °C, which is equal to $n_{surf}/n_{bulk} = \exp(-\Delta G/kT) \sim 1/3$. It can be explained by approximately equal sizes and the same valences of Cr³⁺ and Al³⁺ ions. These elements seem to have the similar values of chemical potential in α -Al₂O₃ lattice that is confirmed by high value of solvability of chromium in alumina [20] and corresponds with little change in concentration of chromium in the samples within the investigated range of temperatures (see Table 4).

For tetravalent ion Ti⁴⁺ $\Delta G = 1.4$ eV that indicates that more energetically favourable state for this impurity is the bulk state. It is probably associated with the high charge that is more effectively screened by the negative oxygen ions in the bulk than on the surface. This circumstance decreases the titanium chemical potential within the lattice and makes this impurity

difficult-to-remove. It also correlates with the results of investigation of chondrite vacuum evaporation that demonstrated the low evaporation degree for TiO₂ as well as for CaO [18].

Conclusions

1. Simple and environmentally benign method for conversion of Al powder of technical purity (99.8 wt. %) into high-purity aluminum oxide with the purity of 99,997 wt. % (total impurity content of about 30 ppm) is developed and tested. The approach is based on hydrothermal oxidation of aluminum and subsequent high-temperature purification of aluminum oxide.

2. Microstructure and chemical compositions of reaction products were studied. It was shown that after 2 hrs annealing at 1750 °C aluminum oxide powder was purified up to 33 ppm, had density of about 1.4 g/cm³ and average particle size of about several microns.

3. Atomistic simulation of impurities segregation on the surface of alumina crystal has been carried out. Simulation results were in good agreement with experimental data and brought to some recommendations for further optimization of proposed technology.

4. It was shown that aluminum oxide, synthesized by means of the proposed method, in general, meets requirements of industrial manufacturers of high purity alumina single crystals.

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