HIGH-PURITY ALUMINA PRODUCTION TECHNOLOGY: HYDROTHERMAL OXIDATION OF ALUMINUM AND FOLLOWING THERMAL TREATMENT

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Abstract

A new technology producing high purity alumina has been developed. Initial reagents for this technology are industrial aluminum micron powder of technical purity (99.8 %) and distilled water. The core of technology is hydrothermal oxidation of aluminum, which is carried out (under about 300 °C and 15 MPa) in special reactor developed for continuous and large-scale production. Conversion degree of aluminum is 100 %. Purity of produced alumina is 99.997 %, i.e. the impurity concentration doesn't exceed 30 ppm. Produced alumina was successfully used for the production of alumina monocrystal.

Key words: *high-purity alumina, hydrothermal oxidation of aluminum, boehmite, hydrogen, sapphire, nanostructured alumina*

1. INTRODUCTION

The lack of efficient and clean technologies for the production of high purity alumina hinders the development of such areas of technological development as optical and semiconductor industries, quantum electronics, energy, instrumentation, etc. High purity alumina is used, for example, for obtaining the high-quality optical ceramics and sapphire, which has a wide range of applications, for example, in the production of LEDs, substrates of chips, laser diodes, implants and artificial joints, microsilica, protective glasses, jewelry, etc. High purity alumina is used in the manufacturing of refractory constructions used in the production of high purity materials. Porous and high-purity materials based on oxides of aluminum are used in such areas like the production of catalysts and sorbents.

To obtain the high-purity aluminum oxide today hydrolysis of aluminum isopropylate (Grinberg et al., 2002), thermal decomposition of aluminum alkoxides (Mekasuwandumrong et al., 2003) and thermal decomposition of aluminum nitrate (Pacewska and Keshr, 2002) are mainly used. Alcohol-based alumina production technology is the main industrially integrated method for obtaining raw material for the production of monocrystallic alumina (Fujiwara et al., 2007). During alcohol-based process high purity alumina is synthesized from metallic aluminum and alcohol: initial aluminum is dissolved in alcohol (usually isopropyl) producing organometallic compound - aluminum alkoxide, then a purification step is carried out to reduce the amount of impurities, after which aluminum hydroxide is produced by hydrolysis (by liquid water or water steam) of alkoxide, aluminum oxide is obtained from aluminum hydroxide by calcination. It can be noted that the methods applied today for the production of high-purity alumina use aggressive chemicals and call the risk to the health and life of operational staff.

Another method of non-metallurgical alumina production is the technology of hydrothermal oxidation of aluminum. Earlier it was shown the possibility of obtaining a boehmite (aluminum oxihydroxide) with high surface area and microporous structure in the hydrothermal reactor of continuous operation at a temperature of about 300 °C and a pressure of about 10 MPa (Shkolnikov et al., 2013). In the process of hydrothermal oxidation of aluminum the technical purity aluminum (aluminum content of about 99.8 %) in the form of powder (micron scale) and distilled water without additional solvent, additives or reagents are used. The degree of conversion in the process of hydrothermal oxidation of aluminum the aluminum was close to 100 % (Shkolnikov et al., 2013).

In this work, we will investigate the possibility of obtaining the high purity alumina by carrying out sequentially the processes of hydrothermal oxidation of aluminum and vacuum-thermal treatment of the product of oxidation. The work will study the changes of structural properties and chemical purity of aluminum oxide obtained during vacuum heat treatment of the product of hydrothermal oxidation.

2. EXPERIMENTAL

Process for producing high purity α-Al_2O_3 in this work was consisted of 4 main steps, which are presented in Fig. 1 (Shkolnikov et al., 2014). The first step is the process of hydrothermal oxidation of aluminum in which at temperature of about 300 °C and pressure of about 10 MPa the boehmite (γ-AlOOH) was produced in accordance with the reaction equation:

$$Al + 2H_2O \xrightarrow{300°C} \gamma\text{-}AlOOH + 1{,}5H_2 \quad (1)$$

From the reactor of hydrothermal oxidation of aluminum the boehmite was removed in the form of boehmite-water suspension. So the next step was the obtaining of dry boehmite by decantation and drying. After that, the boehmite was placed into a muffle furnace for removing the water from crystalline lattice of boehmite and transforming the solid product into gamma or alpha alumina, depending on the temperature:

$$\gamma\text{-}AlOOH \xrightarrow{600°C} 0{,}5\gamma\text{-}Al_2O_3 + 0{,}5H_2O \quad (2)$$

$$\gamma\text{-}AlOOH \xrightarrow{1300°C} 0{,}5\alpha\text{-}Al_2O_3 + 0{,}5H_2O \quad (3)$$

Obtained in a muffle furnace aluminum oxide in the final step was placed into a vacuum furnace for high-temperature purification of aluminum oxide in vacuum. During this process, a final product (α-Al_2O_3) is obtained in accordance with following equation:

$$\gamma\text{-}Al_2O_3 \xrightarrow{>1500°C} \alpha\text{-}Al_2O_3 \quad (4)$$

Samples of boehmite and the products of its thermal treatment were examined using scanning electron microscopy (SEM), x-ray diffraction analysis (XRD), adsorption analysis and chemical composition analysis.

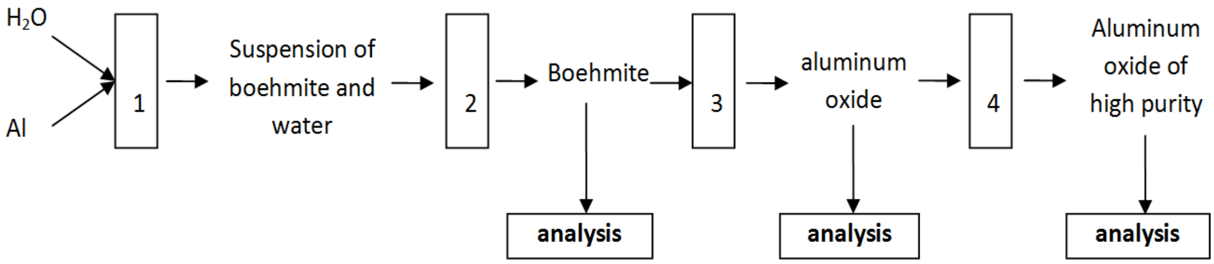


Fig. 1. High purity alumina production process: 1 - hydrothermal oxidation of aluminum (obtaining the oxyhydroxide aluminum - boehmite); 2 - Separation of boehmite from water; 3 - removing the water from boehmite lattice in muffle furnace (obtaining aluminum oxide); 4 - vacuum heat treatment of aluminum oxide.

Surface morphology of the boehmite samples and products of its thermal treatment was studied by scanning electron microscope JEOL JSM-7401F. The phase composition of boehmite and aluminum oxides were studied by x-ray diffraction on diffractometer Thermo ARL XTRA using CuKα radiation (λ=0.15418 nm). Spectra of x-ray diffraction was filmed in the range of angles of 2θ=10-100° with a scanning step of 0.75 °/min. Specific surface of the samples of boehmite and aluminum oxides were studied by low-temperature adsorption of nitrogen on Sorbie 4.1 device. Method of determination of impurity elements in samples of boehmite and aluminum oxides was based on the use of mass spectrometry with inductively coupled plasma (ICP-MS). Before the ionizations the samples were dissolved in special high-purity acids.

3. RESULTS AND DISCUSSIONS

3.1 The properties of product of hydrothermal oxidation of aluminum

SEM image of particles of aluminum powder is presented in Fig. 2. The figure show that in presented work aluminum powder that was used represented the powder with predominantly spherical particles with particle size less than 100 μm.

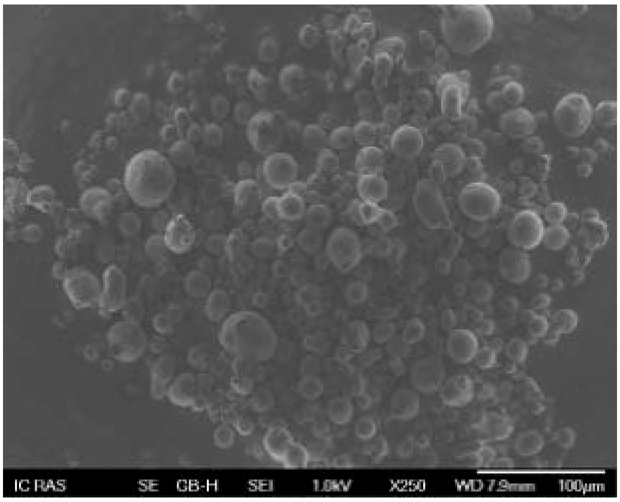


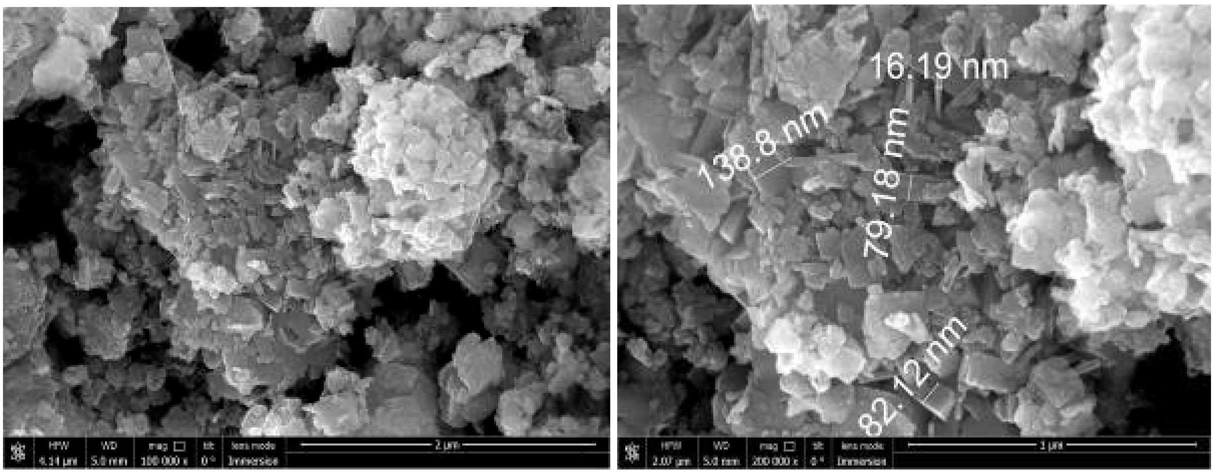
Fig. 2. SEM image of particles of aluminum powder used in the process of hydrothermal oxidation.

Table 1 shows the result of the mass spectrometric analysis of initial aluminum powder. The total content of impurities in the investigated powder was 1452 ppm (not including impurities of silicon). A dominating part of impurities in aluminum accounted for iron, more than 1000 ppm. The content of silicon in the aluminum powders of technical purity, according to the results of other studies, can change from 300 to 700 ppm. So it can be proposed that total impurity content doesn't exceed 2000 ppm that corresponds to the value of technical purity of 99.8 %.

In the reactor of hydrothermal oxidation of aluminum boehmite is formed in accordance with reaction equation (1). XRD analysis of the solid product of hydrothermal oxidation of aluminum confirms that the main crystallographic phase is γ-AlOOH (all peaks obtained on the diffraction pattern correspond to γ-AlOOH) (Shkolnikov et al., 2013). The size of the coherent scattering region, as determined by the Scherrer equation describing the average size of individual crystals, comprised of 30-60 nm.

Hydrothermal oxidation of aluminum powder with particle sizes of about several tens of micron leads to the formation of high-surface solid product with a specific surface area of 83 m^2/g (by BET). From SEM images presented in Fig. 3 it is seen that the product of hydrothermal oxidation of aluminum (boehmite) has a sufficiently large surface area. Figures show that the product represents agglomerated particles with a size of several microns, consisting of single crystals with the size from 10 to 200 nanometers. Such-formed structure of boehmite in combination with the assumption that near the surface of crystals the impurity atoms should be segregated must promote effective impurities removal during the subsequent heat treatment.

From the result of chemical analysis of boehmite it follows that the total content of impurities per gram of substance decreases by more than 2 times compared with the original aluminum (Table 1). This decrease in the content of impurities can be explained first of all by the fact that from one gram of aluminum in accordance with the reaction equation (1) 2.22 grams of boehmite are formed. Therefore, the impurities contained in the original aluminum dissolve in the crystal lattice of boehmite and in case of the absence of impurities in the water the specific content of impurities decreases. In addition, the removal of impurities from boehmite can be facilitated by the fact that in the process of decantation of boehmite produced in the reactor of hydrothermal oxidation of aluminum in the form of aqueous suspension the part of impurities, which dissolves in the water, is removed as a result of draining of water.



a) b)

Fig. 3. SEM images of product of hydrothermal oxidation of aluminum with different scales: (a) 2 μm, (b) 1 μm.

Table 1. The impurity composition in aluminum and boehmite produced from this aluminum.
LoD - the limit of determination for the element.

Element	LoD for Al, ppm	**Al powder**	LoD for AlOOH, ppm	**AlOOH**
Na	25	< LoD	0,9	1,4
Mg	2	12,5	0,3	3,5
Al	-	base	-	Base
K	9	< LoD	1	< LoD
Ca	6	< LoD	1	< LoD
Ti	1,1	6,9	0,6	2,8
V	0,4	55,8	0,2	28,4
Cr	0,4	27,2	0,4	22,0
Mn	0,3	23,2	0,2	10,8
Fe	2	1057	0,8	317
Co	0,0	1,6	0,02	0,76
Ni	0,4	54,1	0,5	21,8
Cu	0,3	5,5	0,4	1,6
Zn	0,3	83,3	0,1	27,9
Ga	0,03	82,4	0,2	34,9
Mo	0,02	2,6	0,1	1,2
W	0,07	0,22	0,09	0,31
Sum, ppm	-	1452	-	476,2

3.2 The properties of alumina

After the synthesis of boehmite it was placed in the muffle furnace to remove water from its crystalline lattice and transfer it to the aluminum oxide. As a result of the transformation of boehmite in a muffle furnace the weight of the solid product was reduced on 14,86 % due to water removal. Structural properties of produced oxide strongly depend on the temperature of muffle furnace heating. Fig. 4 shows the SEM images on which the change in the structure of boehmite heated up to 1100 °C is presented. If boehmite is heated up to 1100 °C it forms aluminum oxide with more less surface area. The crystals of oxide form larger particles, crystals conglomerate with each other.

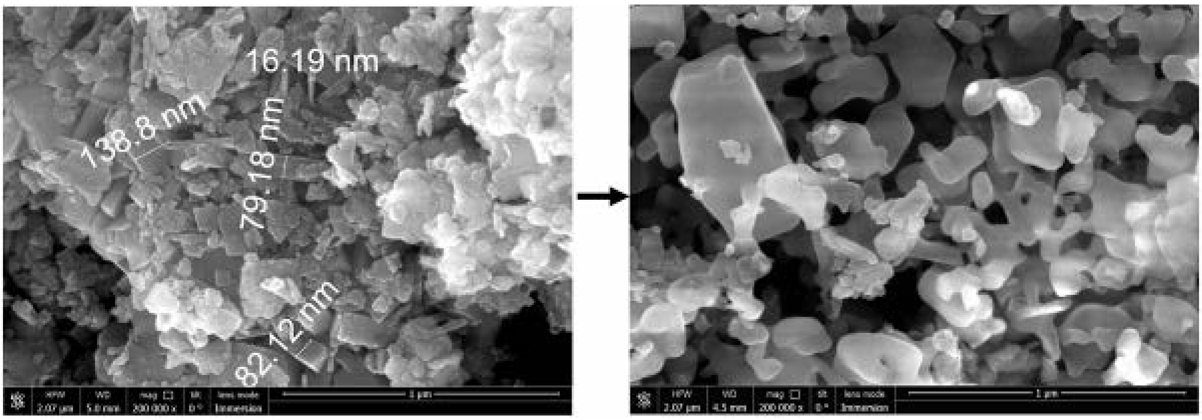
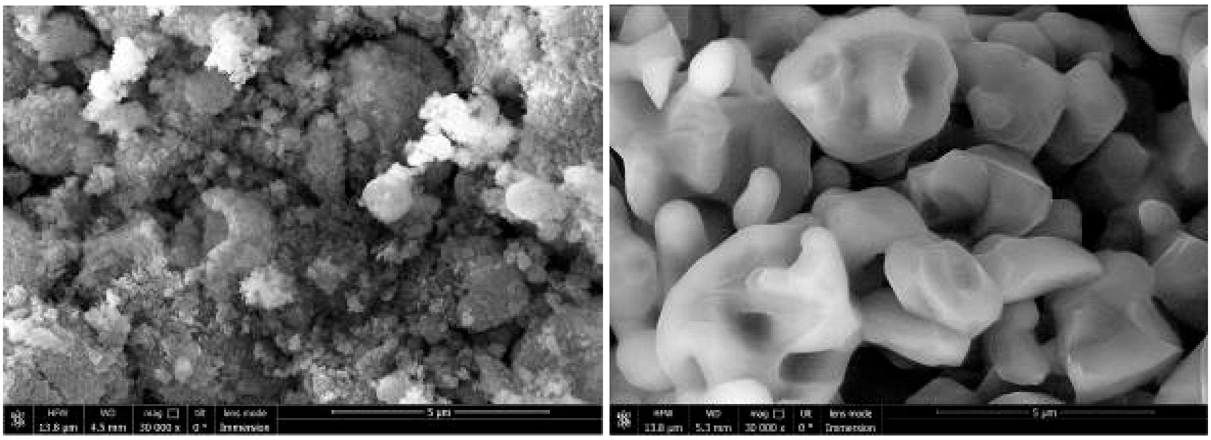


Fig. 4. SEM images (with scale of 1 μm) showing the change in the structure of boehmite heated up to 1100 °C (transformed into aluminum oxide).

After muffle furnace the aluminum oxide was placed into vacuum oven and heated to temperatures 1600-1750 °C. High-temperature thermocouple installed inside the chamber of vacuum oven measured directly the temperature of crucible in which the sample was placed. Fig. 5 shows the images of aluminum oxide obtained in muffle furnace at temperature of 1100 °C, and obtained from it in a vacuum oven at a temperature of 1750 °C α-Al_2O_3. The figure shows how the structure of the oxide changes when it is heated to 1750 °C. Such heat treatment leads to more comprehensive crystal agglomeration, which leads to an increase of particle size. The typical size of the crystals at that temperature increases up to a few microns. The bulk density of powder of aluminum oxide increases on ≈0.3 g/cm^3 and reaches about 1.4 g/cm^3 due to vacuum heating at 1750 °C.



a) b)

Fig. 5. SEM images (with scale of 5 μm) of aluminum oxide obtained in muffle furnace at temperature of 1100 °C (a), and received from it in vacuum oven at temperature of 1750 °C α-Al_2O_3 (b).

Fig. 6 represents the graph of temperature and vacuum pressure inside the chamber of the furnace during the experiment in vacuum oven by the example of experiment with maximum temperature of 1700 °C and the time of maximum temperature maintenance of 6 hours. This figure shows the typical level of vacuum pressure applied in the experiments of vacuum heat treatment of aluminum oxide. Near and during the maintenance of maximum temperature the pressure inside the oven chamber didn't exceed 10^{-4} mm Hg. Figure shows that the relative deterioration of vacuum occurs when temperature approaches the maximum temperature. It was bounded with the sublimation from the refractory of the oven chamber. During the series of experiments performed on vacuum oven it was observed that the higher the maximum temperature of the heating process, the higher the pressure jump when temperature approaches the maximum value.

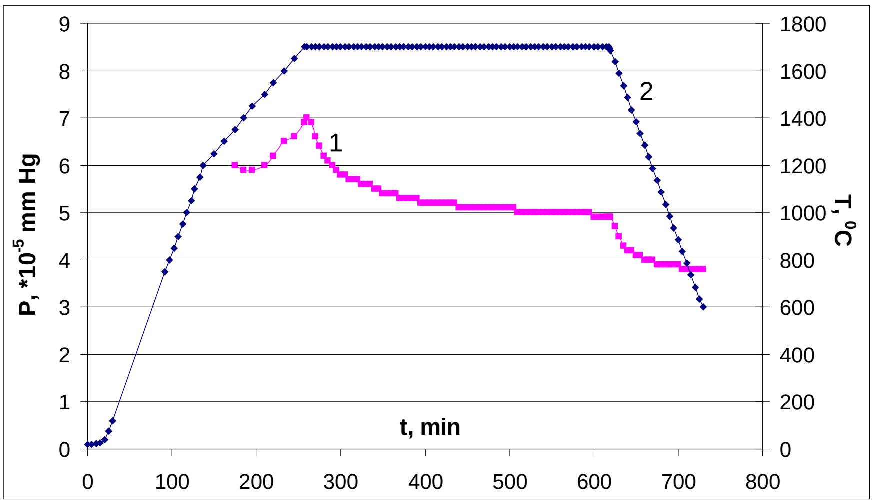


Fig. 6. A graph of temperature and vacuum pressure inside the chamber of the furnace during the experiment in vacuum oven with maximum temperature of 1700 °C and the time of maximum temperature maintenance of 6 hours. 1 – pressure curve, 2 – temperature curve.

The aim of the experiments in vacuum oven was to investigate the dependence of chemical purity of the product on maximum heating temperature and time of maintenance of maximum temperature. Series of experiments in vacuum oven was carried out in temperature range from 1600 to 1750 °C. Inside the vacuum oven in each experiment the aluminum oxide obtained in muffle furnace at temperature of 1100 °C was placed. The results of chemical analysis of the samples of α-Al_2O_3 obtained in vacuum oven at different temperatures and different times of maximum temperature maintenance are presented in Table 2.

From the results of chemical analysis it follows that the content of iron in the sample obtained at 1600 °C and maximum temperature maintenance time of 6 h was 203 ppm that was almost two times more than the iron content in the sample obtained with the same maximum temperature maintenance time, but at a temperature of 1700 °C. Results of chemical analysis also indicate that the increasing of maximum temperature maintenance time from 1 h to 6 h at 1700 °C leads to the reduction of iron from 190 to 109 ppm. From the results of experiments in temperature range of 1600-1700 °C it follows that the content of such impurities as Fe, Mn, Co, Ni, Zn, Ga and Mo with temperature increasing is decreased in produced alumina. The content of such impurities as Ti and V remains almost unchanged after vacuum heating. The content of Mg, Cr and W is increased. The increasing of W was associated with sublimation from the surface of crucible, which was made from wolfram. Such considerable intake of wolfram by the samples obtained in vacuum oven in experiments in temperature range of 1600-1700 °C induced us to continue our following experiments using molybdenum crucible. In this regard, the next experiment at higher temperature of 1750 °C and 2 h maintenance of this temperature was carried out by molybdenum crucible. The result of chemical analysis of the sample obtained in the last experiment confirmed the assumption of wolfram sublimation from the surface of wolframium crucible, because in the sample obtained with molybdenum crucible the content of wolfram was only 6.7 ppm, whereas in the sample obtained at more lesser temperature and maximum temperature maintenance time (1700 °C, 1 h exposure) the content of wolfram was 220 ppm. Minor increasing of W in the sample obtained in last experiment (6.7 ppm) is likely to be bounded with the sublimation from the refractory of the oven chamber. It should be noted that sublimation from the surface of wolframium crucible in experiments in temperature range of 1600-1700 °C could create a local excess of pressure in the area where the sample of aluminum oxide is placed (inside the crucible) that could impede the removal of other impurities from the sample.

In the sample of aluminum oxide obtained at 1750 °C with maximum temperature maintenance time of 2 h the total content of impurities was 33.7 ppm (excluding impurities of silicon). If content of W is not taken into account it can be summarized that the total content of all the impurities was 27 ppm. To identify the content of Si in the sample obtained at 1750 °C it was studied by the mass spectrometer with inductively coupled plasma and laser ablation. From the results of that study it was concluded that the content of Si in the sample obtained at 1750 °C does not exceed 5 ppm. Thus, the chemical purity of the resulting sample of aluminum oxide was at the level of 99,997 %. The resulting value of the total content of impurities satisfies the requirement of manufacturers of synthetic sapphires, however, for the production of high-quality monocrystal of aluminum oxide for such applications as, for example, the production of LEDs, the raw material should meet the concrete requirements for the minimum content of each impurity. In the sample obtained in last experiment these requirements are not satisfied in case of only Fe and theay are close to the limits in case of Cr and V. Bu from the comparison of the results of chemical analysis of samples (table 2) it can be supposed that the content of Fe can be reduced by the increasing either temperature or maximum temperature maintenance time.

Table 2. The results of chemical analysis of the samples of α-Al_2O_3 obtained in vacuum oven at different temperatures (1600, 1700 or 1750 °C) and different times of maximum temperature maintenance (1, 2 or 6 h). LoD - the limit of determination for the element.

Element	LoD, ppm	**1600 °C, 6h**	**1700 °C, 1h**	**1700 °C, 6h**	**1750 °C, 2h**
Na	2	4,8	< LoD	< LoD	< LoD
Mg	1	8,1	8,1	10,1	1,3
Al		Base	Base	Base	Base
K	2	< LoD	< LoD	< LoD	< LoD
Ca	2	< LoD	< LoD	< LoD	< LoD
Ti	1	3,8	4,1	4,1	< LoD
V	0,1	4,9	4,9	5,2	8,5
Cr	1	9,2	9,4	10,3	4,9
Mn	0,2	2,9	2,8	0,6	< LoD
Fe	3	203	190	109	10,2
Co	0,1	< LoD	< LoD	< LoD	< LoD
Ni	0,1	2,4	2	1,99	< LoD
Cu	3	< LoD	< LoD	< LoD	< LoD
Zn	0	< ПО	< ПО	< ПО	< ПО
Ga	0	8,5	6,4	3,6	0,51
Mo	0,04	< LoD	< LoD	< LoD	1,6
W	0,07	110	220	220	6,7
Sum, ppm	-	358	448	364,89	33,7

4. CONCLUSIONS

Presented experimental study has demonstrated the possibility of the obtaining of high purity aluminum oxide by sequentially carrying out the processes of hydrothermal oxidation of aluminum and vacuum-thermal treatment of solid oxidation product (boehmite). The full process producing high purity α-Al_2O_3 consists from the step of hydrothermal oxidation of aluminum, decantation and drying of solid oxidation product, water removal from crystalline lattice of boehmite in muffle furnace and vacuum heat treatment in vacuum oven.

The study of structural properties of boehmite was shown that the product of hydrothermal oxidation of aluminum has nanocrystalline structure. Thermal treatment of the product in vacuum oven at temperatures of 1600-1750 °C resulted in the sintering of crystals with each other and increasing of characteristic size of the crystals up to several microns.

From the results of chemical analysis of the samples it was found that by proposed technology from aluminum with technical purity of 99.8% it is possible to produce high purity aluminum oxide with a purity of 99,997 % (the total content of all impurities of about 30 ppm). In experimental study it was shown that the chemical purity of the final product depends not only on the temperature and time of heat treatment, but also on technological parameters of the process such as, for example, the design and material of the chamber and crucibles.

During experimental work the sample of aluminum oxide that meets the requirement of manufacturers of synthetic sapphires was obtained.

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