

Technology for High Pure Aluminum Oxide Production from Aluminum Scrap

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Abstract. In this study a simple ecologically benign technology of high purity alumina production is presented. The synthesis process consists of three steps) oxidation of aluminum in water at temperature of 90 °C) calcinations of Al hydroxide in atmosphere at 1100 °C) high temperature vacuum processing of aluminum alpha oxide at 1750 °C. Oxidation of aluminum scrap was carried out under intensive mixing in water with small addition of KOH as a catalyst. It was shown that under implemented experimental conditions alkali was continuously regenerated during oxidation reaction and synergistic effect of low content alkali aqueous solution and intensive mixing worked. The product of oxidation of aluminum scrap is the powder of $\text{Al}(\text{OH})_3$. Then it can be preliminary granulated or directly subjected to thermal treatment deleting the impurities from the product (aluminum oxide). It was shown the possibility to produce the high-purity aluminum oxide of 5N grade (99.999 %). Aluminum oxide, synthesized by means of the proposed method, meets the requirements of industrial manufacturers of synthetic sapphire (aluminum oxide monocrystals). Obtained high pure aluminum oxide can be also used for the manufacture of implants, artificial joints, microscalpels, high-purity ceramics and other refractory shapes for manufacture of ultra-pure products.

1. Introduction

High-purity aluminum oxide has a variety of applications and the main are the manufacture of high-quality optics, monocrystal yttrium-aluminium garnets and synthetic sapphires. Synthetic sapphires 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 aluminum oxide is also used for the production of refractory shapes for manufacture of ultra-pure products.

Hydrolysis of aluminum isopropylate [1-2], thermal decomposition of aluminum isopropoxide [3], and thermal decomposition of aluminum nitrate [4] may be used for high-purity alumina manufacturing. Among them, the alcoholate method of aluminum oxide production is the main method which supplies raw material for leucosapphire industry [5]. In this process on the first stage aluminum isopropoxide is synthesized by dissolution of Al in isopropanol. Then aluminum isopropoxide undergoes several purification steps in order to decrease impurity level and then it is hydrolysed by liquid water or water steam. During this process aluminum hydroxide is formed. Further it is calcined to produce alumina. Alcoholate method utilizes aggressive chemicals which cause dangerous pollution.

In all of above mentioned processes, aluminum is used as starting chemical for the production of high-purity aluminum oxide. This is due to the fact that aluminum is a reactive metal, whose industrial production is estimated by tens of millions of tons per year. Aluminum, as a starting material for the production of high-purity aluminum oxide, is more preferable than aluminum oxide, because its purity



can be increased from 99.8 % to 99.99 % during the industrial process of three-layer electrolysis (the Hoops process). The energy cost of electrolytic refining does not exceed the energy cost of the primary aluminum production process (the Hall-Heroult process) [6]. When adding only oxygen to aluminum with a purity of 99.99 % (total content of impurities of 100 ppm), it is theoretically possible to obtain oxide with a purity of about 99.995 % (total content of impurities of 50 ppm), since about 1 kilogram of aluminum produces about 2 kilograms of oxide. However, in practice, the direct oxidation reaction in pure oxygen or water without any additives or catalysts is not so simple [7].

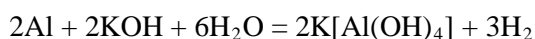
Recently, a method has been proposed for the oxidation of granular aluminum in low-percentage alkali solutions with vigorous stirring, in which the alkali acts as a catalyst for the oxidation process [8]. The producing aluminate under the specific experimental conditions quickly decomposed into aluminum hydroxide and alkali, which then participated in the oxidation of the next portion of aluminum. On the example of potassium hydroxide, the optimal mixing speed, the initial concentration of alkali in the solution (0.1 M), and the weight ratio of the aqueous solution to aluminum ($\alpha = 4$) were determined, which ensure a high conversion of aluminum (more than 80%). Recently, it has also been shown the possibility of purifying aluminum oxide during high-temperature vacuum calcination [9-11]. This process is based on the diffusion of impurities to the surface of the crystal (surface segregation) and their subsequent evaporation [12]. The raw material used was a micron powder of aluminum, the oxidation of which was carried out under hydrothermal conditions at a temperature of about 300 °C and a pressure of 10 MPa [13-15].

In this study a simple and environmentally benign method for conversion of aluminum scrap into high-purity alumina is presented. The synthesis process consists of three steps: i) oxidation of high pure aluminum in water at temperature of 90 °C; ii) calcinations of Al hydroxide in atmosphere at 1100 °C) high temperature vacuum processing of aluminum oxide at 1750 °C.

2. Materials and Methods

In oxidation experiments aluminium in the form of granules with aluminium content of not less than 99.99 % has been used (aluminium grade “A99”) [8]. Experiments on the oxidation of aluminum were carried out in a pilot plant, those description is shown in [8].

The oxidation reaction of aluminum in aqueous solution of potassium hydroxide proceeds according to the following equation:



Produced aluminate is not stable and it is decomposed into a more stable aluminum hydroxide and potassium hydroxide in accordance with the following equation:



Aluminum hydroxide is precipitated at relatively low temperatures. Such precipitation process is used for example in the Bayer process (industrial process producing alumina) when aluminum hydroxide at temperatures about 45-70 °C is precipitated from sodium aluminate aqueous solution. In case of aluminum oxidation in alkaline aqueous solution this reaction leads to the alkali regeneration.

The scheme of method of high-purity $\alpha\text{-Al}_2\text{O}_3$ production is shown in Fig.1. After aluminum oxidation the aluminum hydroxide is decanted and dried. Then it is placed into the muffle furnace and heated in order to remove the crystallized water. During the heating the aluminum hydroxide transforms into $\alpha\text{-Al}_2\text{O}_3$. At the final step, the aluminum oxide obtained by calcination in muffle furnace is placed into the vacuum furnace to provide high-temperature purification. During this process the end product ($\alpha\text{-Al}_2\text{O}_3$) is formed.

A vacuum drying oven VD-53 (Binder GmbH) was used to dry aluminum hydroxide slurry and remove non-bounded water. To remove water from the aluminum hydroxide crystal lattice and to transform it into aluminium oxide a muffle furnace LHT 08/16 (Nabertherm) with molybdenum disilicide heaters was used. To transform the aluminum hydroxide into alumina the 100-ml alumina crucible was used. Crucible with the sample was installed in a central zone of the muffle furnace.

High temperature vacuum purification of aluminium oxide was carried out in a vacuum high-temperature furnace. 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. The useful volume of crucible was about 100 ml (80 mm diameter, 40 mm height, 5 mm wall thickness).

To study the chemical composition of aluminium oxide sample the inductively coupled plasma mass spectrometer ICP-MS, X-2 (Thermo Scientific, USA) was used.

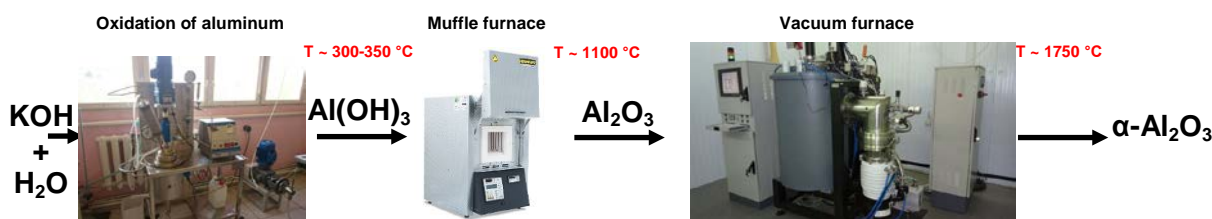


Figure 1. The method of high-purity aluminium oxide production.

3. Results and Discussion

Granulated aluminum was oxidized at $90\text{ }^\circ\text{C}$ in an aqueous solution of potassium hydroxide with a concentration of 0.1 M. The degree of conversion of aluminum was about 80 %. After separation of the resulting aluminum hydroxide from unoxidized aluminum, filtration and drying, and high-temperature vacuum treatment were performed.

The results of mass spectrometric analysis of aluminum oxide sample obtained from aluminum are shown in Table 1. It can be seen from the results that when using high purity aluminum, it is relatively easy to obtain alumina with chemical purity of 99.999 %. Total content of detected impurities is no more than 10 ppm. It should be noted that in this case it is possible to significantly reduce the iron content in the final product. Due to the low content of impurities such as Ti, V and Cr in the original aluminum, the content of these impurities in the final product is minimal and meets the modern requirements of consumers of high-purity alumina. Impurities Ti, V, Cr are the most problematic from the point of view of purification of aluminum oxide by the method of high-temperature treatment [10].

The concentration of alkali metals (K, Na, Li), as can be seen from the results of the study, are less than error value of mass spectrometric analysis. This is due to the diffusion of these impurities to the surface of the crystal, which is also shown in [12]. With increasing temperature, the diffusion rate increases. Therefore, a large temperature of heat treatment leads to a decrease in the content of impurities K, Na and Li in the volume of the crystal and an increase in their concentration at the surface and their evaporation.

4. Conclusion

1. Simple and environmentally benign method for conversion of Al scrap of high purity (99.99 wt. %) into high-purity aluminum oxide with the purity of almost 99.999 wt. % (total impurity content of about 10 ppm) is developed and tested. The approach is based on oxidation of aluminum and subsequent high-temperature purification of aluminum oxide.

2. 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.

3. Described method of high-purity aluminum oxide production was proposed at first. But, in presented work it was tested on the samples in 100 ml crucibles. When the amount of treated sample is increased the evaporated impurities can cause a local extra partial pressure over the sample and so impede its further purification. Therefore, investigation should be continued in order to scale the proposed method of high-purity aluminum oxide production.

Table 1. The results of mass spectrometric analysis of aluminum oxide sample obtained from high-purity granular aluminum.

Element	Error, ppm	Content, ppm	Element	Error, ppm	Content, ppm
Li	0.1	< error	Sb	0.4	< error
Be	0.03	< error	Te	0.03	< error
B	0.3	< error	Cs	0.004	< error
Na	6	< error	Ba	0.08	< error
Mg	2	< error	La	0.02	0.74
Al	Base	Base	Ce	0.04	0.31
K	1	3.2	Pr	0.004	0.040
Ca	6	< error	Nd	0.04	0.15
Sc	1	< error	Sm	0.01	0.019
Ti	1	< error	Eu	0.002	< error
V	0.6	2.4	Gd	0.02	< error
Cr	1	< error	Tb	0.004	< error
Mn	0.2	< error	Dy	0.01	< error
Fe	9	< error	Ho	0.004	< error
Co	0.1	< error	Er	0.01	< error
Ni	1	< error	Tm	0.004	< error
Cu	1	< error	Yb	0.004	< error
Zn	1	< error	Lu	0.004	< error
Ga	0.3	< error	Hf	0.2	< error
As	0.1	< error	Ta	0.01	< error
Se	2	< error	W	0.03	0.76
Rb	0.04	< error	Re	0.004	< error
Sr	0.09	< error	Ir	0.004	< error
Y	0.02	< error	Pt	0.004	< error
Zr	0.6	< error	Au	0.004	< error
Nb	0.04	< error	Hg	0.06	< error
Mo	0.07	1.2	Tl	0.004	< error
Rh	0.2	< error	Pb	0.06	< error
Pd	0.1	< error	Bi	0.01	< error
Ag	0.04	< error	Th	0.01	0.025
Cd	0.03	< error	U	0.004	< error
Sn	0.3	< error	The sum	36.04	8.86

5. Acknowledgements

The study was supported through a grant of the Russian Science Foundation (project No. 14-50-00124).

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