Densification of Porous Aluminum Oxide Powder by Plasma Arc Treatment

A V Grigorenko* and M S Vlaskin

Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
*E-mail: presley1@mail.ru

Abstract. Present paper is devoted to study of the process of aluminum oxide densification by plasma arc in experimental plant. Aluminum oxide was produced in three stages: oxidation of aluminium chips in glass reactor; the treatment of oxidation product in muffle furnace and aluminum oxide densification in plasma arc. It was shown that the density of aluminum oxide after plasma arc treatment increases from about 1.0 to 1.9 g/cm³. By microstructure analysis it was shown that the product after plasma arc treatment obtained the spherical form of crystals due to the melting of aluminum oxide particles and collisions of the particles with each other. Described method is proposed to be used for mass-production of dense aluminum oxide powders.

1. Introduction
Aluminum oxide is one of the world’s most plentiful substances[1]. It is one of the highest volume inorganic chemicals sold in the world today. Aluminum oxide is used in a large number of applications, ranging from water treatment and toothpastes to fire-stable plastics. Aluminum oxide has been used for many years by the ceramic industry. It is also used in optical and semiconductor industry, quantum electronics, electric-power industry, instrument engineering, etc. Porous and pure aluminum oxides and hydroxides are used to manufacture catalysts, adsorbents and heat-resistance materials [2].

One of the modern high-tech fields of aluminum oxide application is the manufacture of synthetic sapphire. 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. The raw for synthetic sapphire manufacturing is high-purity aluminum oxide. High-purity aluminum oxide itself has a variety of applications, among them there are the manufacture of high-quality optics, yttrium-aluminium garnets and production of refractory shapes for manufacture of ultra-pure products.

There are a number of methods to produce high-purity aluminum oxide. Today, hydrolysis of aluminum isopropylate[3-4], thermal decomposition of aluminum isopropoxide[5], and thermal decomposition of aluminum nitrate [6] are often used. High-purity aluminum oxide can be obtained by hydrothermal oxidation of aluminum[7-8] and subsequent high temperature purification of solid oxidation product [9-10]. The purification process is based on the diffusion of impurities to the surface of the crystal (surface segregation) and their subsequent evaporation at high temperatures (1700-1900 °C) [11]. In our previous work we proposed a method for conversion of aluminum scrap into high-purity alumina based on such purification [12].

But, in all above mentioned methods the product has a very low bulk density. Low bulk density decrease the efficiency of the process of synthetic sapphire growing that usually lasts for several days. Thus, the densification of aluminum oxide is needed to increase the loading of aluminum oxide into the crucible of sapphire-growing furnace. For this purposes the hot isostatic pressing is usually used.
Main disadvantages of this method are low productivity and the necessity of adjusting the press-form to the size of crucible of sapphire-growing furnace.

In present study we will study the process of aluminum oxide densification by plasma arc in experimental plant. The change of bulk density and the microstructure change are under investigation.

2. Materials and methods
Preparation of dense aluminum oxide was carried out in accordance with the process scheme shown in fig. 1. Full process included three stages: aluminum oxidation in glass reactor; aluminum hydroxide treatment in muffle furnace and aluminum oxide densification in plasma arc.

Aluminum in the form of chips with aluminum content of not less than 99.995% (UC Rusal company) was used as starting material. Aluminum oxidation was carried out in glass reactor described in [13-14]. Aluminum was oxidized in 0.1 M KOH aqueous solution with vigorous stirring at temperature of 90 °C. After aluminum oxidation the produced aluminum hydroxide is decanted and dried.

Aluminum hydroxide was placed into the muffle furnace and heated up to 1300°C in order to remove the crystallized water and produce stable form of α-Al2O3. To remove water from the crystal lattice of aluminum hydroxide and to transform it into aluminium oxide a muffle furnace LHT 08/16 (Nabertherm) was used.

At the last stage aluminum oxide was processed in original plasmatron. The scheme of plasmatron is shown in fig. 2. It included a tungsten cathode, an interelectrode insert (nozzle), and an anode parts. The ignition of an arc plasma occurred in an argon medium at a voltage of 30 V and a current of 250 A. The argon rate was 0.8 g/s. Aluminum oxide powder was introduced into the plasma arc with the help of argon. For this purpose a special bunker with fluidized bed was used before plasmatron. To collect the resulting products under the anode, a water bath was installed in which the products were collected and cooled.

Surface morphology of solid products was studied on JEOLJSM-7401F scanning electron microscope (SEM). Samples were placed into the microscope on carbon substrate. The shooting was carried out at 1 kV accelerating voltage. Phase composition of product was studied by X-ray diffraction (XRD) using Thermo ARL XTRA diffractometer using CuKα radiation (λ=0.15418 nm).

Figure 1. Process scheme for the production of dense aluminum oxide

Figure 2. The scheme of plasmatron. 1 – cathode, 2 – nozzle, 3, 4 – anodes

3. Results and discussion
Due to X-ray analysis it was established that the dominant phase in solid oxidation product was Al(OH)3, which was represented by two modifications – gibbsite and bayerite. Fig. 3 shows microstructure of solid oxidation product at different scales. Solid oxidation product represents the
powder which is consisted from crystals with rectangular form. The size of single crystal is about several microns.

Fig. 4 shows the microstructure of the product of thermal treatment in muffle furnace at 1300°C. As it can be seen, as water of crystallization escapes from the crystals during heat treatment process the surface of the crystals becomes rougher resulting in the formation of pores with a size of several tens of nm. At the same time the product kept the rectangular form of macro crystals.

Fig. 5 shows the microstructure of the product obtained after densification in plasma arc. It can be seen that the product obtained the spherical form of crystals. It is probably due to the melting of aluminum oxide in plasma arc. In plasma arc aluminum oxide particles melt and take the collisions with each other thus growing. Fragments of non-melted particles with the structure similar to the structure of the product of thermal treatment in muffle furnace (shown in fig. 4) are also can be seen in fig. 5. It can be explained by short time of flight of aluminum oxide particles inside the hot zone of plasmatron. That time was about 0.1 sec.

X-ray analysis showed that both the product of thermal treatment in muffle furnace at 1300°C and the product obtained after densification in plasma arc represent pure $\alpha$-$\text{Al}_2\text{O}_3$. The bulk density of the product of thermal treatment in muffle furnace at 1300°C was almost the same as for oxidation product and equaled to about 1.0÷1.1 g/cm$^3$. The bulk density of the product shown in fig.5 (obtained after densification in plasma arc) was about 1.9 g/cm$^3$.

Figure 3. Microstructure of solid oxidation product (at different magnification)
Additional experiments were carried out with the rods made from aluminum oxide. These preliminary prepared rods were supplied into the hot zone of plasmatron through the hole in the nozzle. The aim of that experiment was to increase the time of plasma arc treatment to several seconds. In the hot zone of plasmatron the end of the rod was blown by hot ionized argon that led to the melting of aluminum oxide and dripping. The resulting product represents compact balls and it is shown in fig. 6. The density of each ball was about 3.1±0.3 g/cm$^3$. 

Figure 4. Microstructure of product produced in muffle furnace (at different magnification)

Figure 5. Microstructure of product produced in plasma arc (at different magnification)
Figure 6. The product of plasma arc treatment of aluminum oxide rods supplied into the hot zone through the nozzle of plazmatron. Time of treatment is about several seconds.

4. Conclusion
The opportunity for aluminum oxide densification by plasma arc was experimentally shown. It was shown that the density of aluminum oxide increases in almost two times after plasma arc treatment at a treatment time of about 0.1 sec. At treatment time of about several seconds the density of aluminum oxide particles reaches 3 g/cm$^3$. By microstructure analysis it was shown that the product after plasma arc treatment obtained the spherical form of crystals due to the melting of aluminum oxide particles and collisions of the particles with each other. Such method can be used for mass-production of dense aluminum oxide powders including high-purity powder for sapphire production.

5. References
[1] McLeod C T, Kastner J W, Carbone T J and Starr J P 2008 Proceedings of the Conference on Raw Materials for Advanced and Engineered Ceramics: Ceramic Engineering and Science Proceedings: John Wiley & Sons, Inc.) pp 1233-43
[2] Lisitsyn A V, Dombrovsky L A, Mendeleyev V Y, Grigorenko A V, Vlaskin M S and Zhuk A Z 2016 Near-infrared optical properties of a porous alumina ceramics produced by hydrothermal oxidation of aluminum Infrared Physics & Technology 77 162-70
[3] Grinberg E E, Saradzhev V V, Levin Y I and Ryabenko E A 2002 Preparation of Fine Alumina Powders by Hydrolysis of Aluminum Isopropylate Russian Journal of Applied Chemistry 75 245-7
[4] Khishigbayar K E, Moon Y G, Bae E J, Shim K B and Kim C J 2013 Impurity control with the precise measurement of alumina powders synthesized by hydrolysis method Journal of Ceramic Processing Research 14 168-71
[5] Mekasuwandumrong O, Silveston P L, Praserthdam P, Inoue M, Pavarajarn V and Tanakulrungsank W 2003 Synthesis of thermally stable micro spherical $\gamma$-alumina by thermal decomposition of aluminum isopropoxide in mineral oil Inorganic Chemistry Communications 6 930-4
[6] Pacewska B and Keshr M 2002 Thermal transformations of aluminium nitrate hydrate Thermochimica Acta 385 73-80
[7] Vlaskin M S, Shkol’nikov E I, Lisitsyn A V and Bersh A V 2010 Thermodynamic calculation of the parameters of a reactor for oxidizing aluminum in wet saturated steam Thermal Engineering 57 794-801
[8] Vlaskin M S, Dudoladov A O, Buryakovskaya O A and Ambaryan G N 2018 Modelling of aluminum-fuelled power plant with steam-hydrogen enthalpy utilization International Journal of Hydrogen Energy
[9] Vlaskin M S, Grigorenko A V, Zhuk A Z, Lisitsyn A V, Sheindlin A E and Shkol’nikov E I 2016 Synthesis of high-purity $\alpha$-Al2O3 from boehmite obtained by hydrothermal oxidation of aluminum High Temperature 54 322-9
[10] Zhuk A Z, Vlaskin M S, Grigorenko A V, Kislenko S A and Shkolnikov E I 2016 Synthesis of high-purity $\alpha$-Al$_2$O$_3$ from boehmite by high temperature vacuum treatment Journal of Ceramic Processing Research 17 910-8

[11] Kislenko S A, Vlaskin M S and Zhuk A Z 2016 Diffusion of cation impurities by vacancy mechanism in $\alpha$-Al$_2$O$_3$: Effect of cation size and valence Solid State Ionics 293 1-6

[12] Ambaryan G N, Vlaskin M S, Shkolnikov E I and Zhuk A Z 2017 Technology for High Pure Aluminum Oxide Production from Aluminum Scrap IOP Conference Series: Materials Science and Engineering 250 012044

[13] Ambaryan G N, Vlaskin M S, Dudoladov A O, Meshkov E A, Zhuk A Z and Shkolnikov E I 2016 Hydrogen generation by oxidation of coarse aluminum in low content alkali aqueous solution under intensive mixing International Journal of Hydrogen Energy 41 17216-24

[14] Dudoladov A O, Buryakovskaya O A, Vlaskin M S, Zhuk A Z and Shkolnikov E I 2016 Generation of hydrogen by aluminium oxidation in aqueous solutions at low temperatures International Journal of Hydrogen Energy 41 2230-7