Purification of fused alumina by high temperature calcination in vacuum

G E Belyaev, A V Grigorenko, M S Vlaskin, I A Lipatova, E I Shkolnikov, A Z Zhuk
Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow, 125412, Russia
E-mail: belyaev.g@yahoo.com

Abstract. The aim of present study was the investigation of purification efficiency of industrial white fused alumina at high-temperature calcinations, in vacuum. Three powder samples of alumina with different initial purity and particle size distribution were studied. The impurities amount in the white fused alumina powder decreased by factor 10 after vacuum calcinations. White fused alumina samples were almost completely cleared of Na, Mg, K, Mn, Cu and Zn. The iron content in the studied samples decreased by factor 8–10. Comparison of the granulometric composition and specific surface area of samples, showed that samples look like sets of porous grains with the average sizes between 16–60 µm. In turn, porous grains are composed of dense micro-particles with a characteristic size of 0.4–0.7 µm. The specific surface area of grains lies in the range 2.8–3.3 cm²/g. Relatively high rate of purification takes place due to porous structure and high surface area of the samples.

1. Introduction
Fused alumina is a refractory and chemically resistant super hard material based on aluminum oxide (Al₂O₃). White fused alumina consists of α-oxide Al₂O₃ (98–99%) and impurities (1–2%) in the form of high alumina sodium aluminates and other minerals. Manufacture white fused alumina is a process of alumina arc-melting resulting in γ-Al₂O₃ is completely transformed to α-Al₂O₃.

Chemical purity of fused alumina is one of the fundamental properties that determine its consumer quality and the market value. White fused alumina of high chemical purity is used for the manufacture of abrasive materials, high-density corundum refractory, for responsible lining units of thermal units operating in a variable oxidation-reduction (redox) medium or reducing gas environment, and in particular for reactors for the production of technical carbon. The result of the use of high chemical purity white fused alumina is an increase in heat resistance, erosion resistance, strength and reduction of porosity, reduction of production defect in the process of heating the refractory and subsequent cooling throughout the temperature range of the furnace. Therefore, obtaining high chemical purity corundum is an urgent and practically significant task. In recent works of the JIHT RAS, the possibility of purification of α-aluminum oxide to the level of 99.997% by high-temperature calcinations in vacuum was demonstrated [1,2].

The aim of present study was the investigation of purification efficiency of industrial white fused alumina by a similar method, i.e. by high-temperature vacuum calcinations.
2. Experimental set up and measurement methodology

White fused alumina powder samples were obtained by crushing of a 6-ton ingot. The ingot was obtained by crystallization of the molten fused alumina in the mold in the factory LLC RUSAL Boksitogorsk. In the process of solidification of corundum melt, several areas are formed in the ingot. Chemical composition and structure of areas differ significantly [3]. After cooling, impurities are concentrated near the center of the ingot. Crystals of submillimeter-sized oxide with micro-inclusions of aluminates are formed in the lower part of the ingot. Dendrite structures are formed on the lateral surfaces of the ingot.

In the experiments, three powder samples of white fused alumina were studied: sample I – from the crust formed on the surface of the fused alumina ingot as a result of cooling; sample II – from the middle part of the fused alumina ingot; sample III – from the lower part of the ingot. Vacuum heat treatment of samples was carried out at the NIKA–M60 plant manufactured by FSUE “EZAN”. The furnace had a cylindrical tungsten heater and cylindrical molybdenum shields situated around the heater. The scheme of the furnace is shown in figure 1. A cylindrical molybdenum crucible (8) was installed inside the furnace. A crucible had following dimensions: 740 mm – height, 300 mm – diameter, wall thickness – 10 mm.

![Figure 1. The scheme of the vacuum furnace (1, 4, 6 – thermal shields; 2, 3 – external and internal walls; 5 – furnace bottom; 7 – crucible supporting structure; 8 – molybdenum crucible; 9 – gas supply unit) and calcination parameters (1 – temperature, 2 – pressure)](image)

Increasing the heat treatment temperature of dispersed corundum activates two competing processes. First, the increase in temperature is accompanied by an increase in the rate of diffusion and sublimation, and second, activated grains sintering, leading to an increase in the size of micro-particles. This in turn increases the diffusion path of impurities and reduces the specific surface area of evaporation. According to [1] at 1600°C a significant reduction in iron concentration takes about 10 hours due to the relatively low diffusion rate. Despite the exponential growth of the diffusion coefficient and the partial pressures growth of the substance components at a higher temperature, after heat treatment at 1900°C iron concentration was higher than after heating to 1750°C.

The temperature of the crucible was measured by an optical pyrometer Kelvin Compact D2300 through a quartz viewing window in the upper lid of the vacuum chamber and a central hole in the thermal shield (1). Additionally, the temperature of the crucible (8) was controlled...
by a thermocouple, which was mounted in the bottom of the crucible. At temperatures above 1000°C, thermocouple and pyrometer readings differed by less than one degree.

The mass of each sample was 30 grams. Molybdenum rectangular shape cuvettes with samples were placed near the center on the bottom of molybdenum crucible.

The chemical composition of fused alumina samples before and after heat treatment was determined by a mass spectrometer with inductively coupled plasma (ISP-MS, X-2 Thermo Scientific, USA) with preliminary dissolution of the substance in a mixture of $\text{H}_2\text{SO}_4$ and $\text{H}_3\text{PO}_4$ [4].

Granulometric analysis of fused alumina samples was studied by laser diffraction using “Fritsch Analysette 22” based on a semiconductor laser ($\lambda = 650$ nm, 7 mW). Measurement range of the grain size of the powders was 0.3–600 µm. The relative error of the integral distributions was 5%.

The microstructure of the samples was studied using a scanning electron microscope JEOL JSM-7401F. Parameters of porous structure of sample grains were found by two independent methods and their combination:

- differential pore distributions over the sample radii before and after high-temperature treatment were obtained by limited adsorbed evaporation (benzene) [5,6];
- a total porosity (specific pore volume) of grains was determined by the method of their saturation with wetting liquid (decane) with the subsequent determination of its mass and conversion to the volume coinciding with the pore volume;
- the combination of both methods determined the typical average size of the micro-particles that make up the sample granule.

3. Results and discussion

The results of chemical analysis of fused alumina samples before and after high-temperature vacuum treatment and the parameters of the porous structure of the sample grains are presented in table 1.

Results of mass spectrometry analysis of chemical composition of fused alumina powders (table 1) show that the after calcination total impurity content decreased by about ten times, and the purity of the fused alumina is higher than 99.91%. Comparison of the data of optical measurements of particle size distribution and porometry data indicate that the alumina grains have a porous structure and are composed of micro-particles with a characteristic size of about 0.5 microns. Heat treatment of samples is accompanied by sintering, which leads to a decrease in porosity and specific surface area of the samples (table 1 and figure 2).

The impurities in fused alumina can be divided into three groups. The first group of elements (table 1) Na, K, Fe with a relatively high initial concentration in the samples 500–1700 µg/g. After vacuum calcination their content decreased significantly – by factor 7 and more.

The second group of elements includes elements – Cu, Mg, Mn and Zn. Their initial content was relatively small 20–60 µg/g. After calcinations their content decreased to the detection threshold.

The third group of elements are calcium and gallium 200–500 µg/g and 110–130 µg/g, respectively. The quantity of these elements was quite high in the initial samples and after heat treatment their concentrations changed very slightly.

The features of impurity release can be interpreted by well-known models of sublimation for multi-component mixtures [7–9]. Sublimation refining of porous alumina consists of the following main stages:

(i) Diffusion of impurities to the surface of a compact micro-particle followed by evaporation (sublimation) from the surface of the micro-particle;
Table 1. Mass spectrometry data on chemical composition in [µg/g] (DT – detection threshold) and porometry data before and after vacuum calcination of alumina powders.

| Elements | Sample I | | Sample II | | Sample III | |
|----------|----------|---|----------|---|----------|---|
|          | DT       | before | after | before | after | before | after |
| Na       | 5        | 1513   | <DT   | 3919   | <DT   | 3064   | <DT   |
| K        | 6        | 464    | <DT   | 1225   | <DT   | 961    | <DT   |
| Fe       | 6        | 1720   | 255   | 2131   | 283   | 1077   | 90    |
| Cu       | 1        | 20.1   | <DT   | 5.2    | <DT   | 90     |
| Mg       | 1        | 19.4   | <DT   | 27.4   | 3.9   | 18     | <DT   |
| Mn       | 0.3      | 18.5   | <DT   | 87.4   | 1.2   | 81.9   | 1.2   |
| Zn       | 1        | 59.3   | <DT   | 20.2   | <DT   | 13.6   | <DT   |
| Ca       | 16       | 235    | 207   | 474    | 474   | 351    | 353   |
| Ga       | 0.2      | 118    | 86.9  | 133    | 103   | 124    | 114   |
| Total sum| 4181     | 558    | 8056  | 885    | 5710  | 569    |

Parameters of grains porous structure

| Average size of the grains (µm) | 16 | 25 | 32 | 32 | 64 | 65 |
|---------------------------------|----|----|----|----|----|----|
| Specific pore volume (cm³/g)    | 0.10 | 0.11 | 0.14 | 0.09 | 0.11 | 0.06 |
| Specific surface area 10⁴(cm²/g) | 2.8 | 2.5 | 2.2 | 2.5 | 3.3 | 1.3 |
| Micro-particle average size(µm) | 0.53 | 0.60 | 0.68 | 0.60 | 0.46 | 1.27 |

(ii) The Knudsen diffusion of the impurities through the pores in a grain body to its surface and further;

(iii) The Knudsen diffusion of the impurities through the layer of grains to the outer surface of a powder sample.

The intensity of the impurity exit from the sample is determined by the diffusion rates of the impurity and the evaporation rate of the impurities from the surface of the micro-particle. The intensity of the latter process is determined by the values of the equilibrium pressure of the impurity vapor at a given temperature and the current concentration of the impurity on the micro-particle surface.

One can estimate diffusion coefficients – $D$ [10] and characteristic diffusion times $t$ for a distance of about the diameter of the micro-particles $\approx 0.5$ µm at calcinations temperature $\approx 1750$ °C. For $N$, $D \approx 7.4 \times 10^{-8}$ cm²/s and $t \approx 30$ s, for Fe – $D \approx 6 \times 10^{-13}$ cm²/s, $t \approx 1.1$ hours. On the other hand, the estimate of Knudsen diffusion $D_K$ for the pore diameter $\approx 0.2$ µm gives a value for iron $\approx 0.6 \times 10^{-8}$ cm²/s, for sodium $\approx 1.35 \times 10^{-8}$ cm²/s. Thus, the Knudsen diffusion coefficient $D_K$ for iron is 5 orders higher than the diffusion coefficient of iron in compact oxide – $D$. Consequently, the rate of release of iron release is limited by diffusion in a compact micro-particle and the rate of sublimation from the surface of the micro-particle.

From the comparison of chemical analysis results and porometry data (table 1), it follows that the highest release of iron was observed for the sample with the most developed surface – sample III. Consequently, the release of iron was limited by sublimation from the surface of microparticles. It should be emphasized that for the characteristic diffusion length corresponding to the grain size ($\approx 10$ µm), the diffusion time for iron impurities will be about 100 hours. It
follows that significant release of iron impurities is observed due to the fact that the alumina grains are composed of micro-particles ($\sim 0.5 \mu m$) i.e. the characteristic diffusion time in a solid micro-particle is comparable with the time of the experiment.

The Knudsen diffusion coefficient for sodium has the same order of magnitude as the diffusion coefficient of sodium in a continuous oxide. Thus, the diffusion rate of is high enough and release rate of $Na$ is controlled by the rate of evaporation from the surface of the micro-particles. It can be proposed the same situation takes place in case of $K$ release. Unfortunately? We could not find necessary data for direct estimations.

Diffusion coefficients of $Cu$ and $Mg$ in compact alumina are higher than that for iron [10,11]. It is proposed that release of these elements is controlled by sublimation.

Very weak influence of vacuum calcination on calcium and gallium concentration (the third group of elements) is probably due to the fact that these elements are in the state of inert refractory oxides. The melting point of calcium oxide $\approx 2570^\circ C$, gallium oxide – Ga$_2$O$_3$ in the crystal lattice of corundum is not less than $\approx 1806^\circ C$ [12], i.e. significantly higher than the heat treatment temperature $\approx 1750^\circ C$.

4. Conclusion
It is proposed a simple way to increase the purity of white fused alumina by calcinations at $\approx 1750^\circ C$ in vacuum $\sim 10^{-5}$ torr. After calcination, the total content of impurities in the samples decreased tenfold. The purity of the fused alumina changed from 99.2–99.6% to 99.91–99.95%.

Comparison of the data of optical megranulometry of samples and data of porometry shows that the grains of powder samples have a porous structure and are composed of micro-particles

Figure 2. Microphotographs of fused alumina grains in sample I before (a) and after (b) heat treatment and corresponding size distributions.
with a characteristic size of about 0.5 microns. As a result, the characteristic diffusion time in a micro-particle is comparable to the time of the experiment. Increasing the heat treatment temperature of the porous alumina activates two competing processes. The increase of temperature is accompanied by an increase in the rate of diffusion and sublimation. On the other hand, the increase of calcination temperature activates sintering of microparticals, thus increasing their sizes, reducing their specific surface and reducing the release of impurities.

The presented results can be used for high purity alumina production on an industrial scale.

Acknowledgments
The authors express their gratitude for the samples of white fused alumina provided to the managing Director A.A. Golovanov of LLC “RUSAL Boksitogorsk”.

References
[1] Zhuk A Z, Vlaskin M S, Grigorenko A V, Kislenko S A and Shkolnikov E I 2016 Journal of Ceramic Processing Research 17(9) 910–918
[2] Kislenko S A, Vlaskin M S and Zhuk A Z 2016 Solid State Ionics 293 1–6
[3] Garshin A P and Fedotova S M 2008 Abrasive materials and tools. Production technology (Saint-Petersburg: Polytechnic University)
[4] Khvostikov V A, Karandashev V K and Burmii Z P 2015 Inorganic Materials 51(14) 1410–1415
[5] Shkolnikov E I, Sidorova E V, Malakhov A O, Volkov V V, Julbe A and Ayra A 2011 Adsorption 17(6) 911–918
[6] Yanilkin I V et al 2015 Journal of Applied Chemistry 7 1157–1167
[7] Bokshtein S Z and Fedotova S M 1971 Structure and properties of metallic alloys (Moscow: M. "Metallurgiya")
[8] Powell A, Van Den Avyle J, Damkroger B, Szekely J and Pal U 1997 Metall. Mater. Trans. 38(B) 1227–1239
[9] Malek K and Coppens M O 2003 The Journal of Chemical Physics 119 2801
[10] Doremus Robert H 2006 J. Appl. Phys. 100 101301
[11] Harding J H, Atkinson K J W and Grimes R W 2003 J. Am. Ceram. Soc. 84(4) 554–559
[12] Maslov V N, Krimov V M, Kalashnikov E V and Nikolaev V I 2014 Materials Physics and Mechanics 21 194–199