Purification of corundum by calcination under controlled reducing conditions

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Abstract

The alkaline impurities detract from the mechanical properties of corundum materials, specially at high temperatures. So it is important that they are minimized. This paper describes a new purification method of aluminas by calcination at high temperatures ($>1200°C$) in controlled reducing atmospheres ($P_{O_2} \sim 10^{-15}$ atm). Under these conditions, alkaline impurities are removed by reduction to volatile species. Over 95% of Na_2O existing in the alumina can be removed in this way. SiO_2 and Fe_2O_3 can also be removed with these treatments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Calcination; Powders-gas phase reaction; Purification

1. Introduction

Most commercially available alumina originates from the Bayer process: digestion of bauxite by hot NaOH under pressure to afford soluble sodium aluminate, followed by precipitation of Gibbsite.[1] Thermal treatment of this gibbsite at 900°C produces amorphous alumina, which can be transformed in α-Al_2O_3 (corundum) by calcination at high temperatures.

The corundum obtained in this way contains significant quantities of impurities (in particular, 0.1–0.7% wt of Na_2O). Most of these impurities are concentrated in corundum grain borders, and leads to a severe deterioration of the high temperature mechanical properties of corundum products.[2]

For good high-temperature performance, corundum must be purified, or produced in the first instance from pure alumina. Leaching the amorphous alumina with water before calcination only reduces its impurity content in a limited extent. High-purity alumina can be produced by sol-gel methods,[3,4] but their industrial implementation is hampered by their high cost and their use of highly pollutant solutions. The alternatives are to purify either Bayer amorphous alumina or corundum obtained directly from unpurified alumina.

According to the Ellingham diagram,[5] alumina is more stable than Na_2O under reducing conditions (Fig. 1). At 1300°C, for example, atmospheres in which the partial pressure of oxygen (P_{O_2}) is less than 10^{-10} atm reduce Na_2O, whereas Al_2O_3 is unaffected until P_{O_2} falls below 10^{-26} atm. In this article we describe how this difference can be used to obtain high purity corundum in one step by calcination of amorphous alumina in an atmosphere that reduces impurities to volatile species, or to purify corundum by calcination under the same conditions.
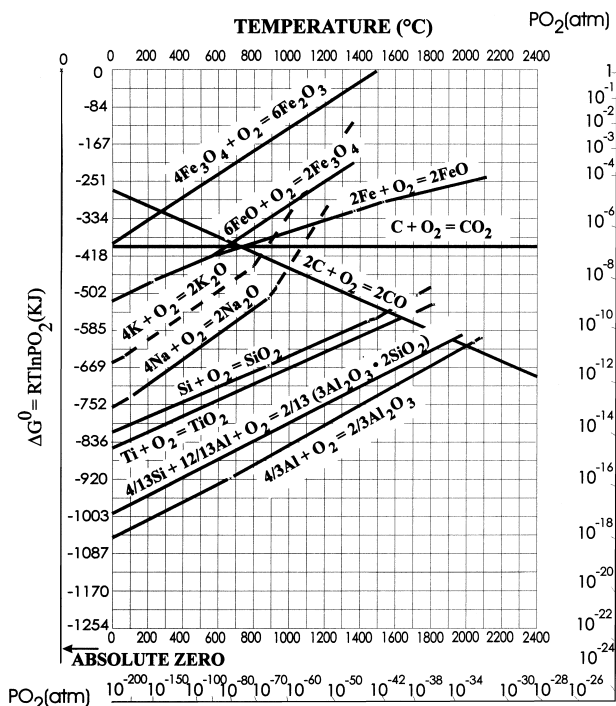
2. Experimental

Amorphous alumina was supplied by Alcoa (San Ciprián, Lugo, Spain).

Reducing calcinations were performed for up to 5 h at temperatures of 900–1400°C both in nitrogen at atmospheric pressure and under vacuum ($P = 10^{-4}$ atm), in a Pyrox H1-16L/17 controlled atmosphere graphite-lined furnace equipped with a vacuum pump.

Samples in ZrO_2 crucibles were loaded in the furnace, pressure was reduced to below 10^{-4} atm and then restored to 1 atm with nitrogen (N_2, Air Liquide N50; $P_{O_2} = 2 \times 10^{-6}$ atm). In the experiments in nitrogen at atmospheric pressure, heating was started at this point. In the calcinations carried out under vacuum, the pressure in

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Fig. 1. Ellingham diagram.[5]

Table 1
Major impurity contents (wt%) of amorphous alumina (A) and of corundum produced by reducing calcination of amorphous alumina for 1 h at 1400°C under vacuum (10^{-4} atm) (B) or in nitrogen at 1 atm (C)

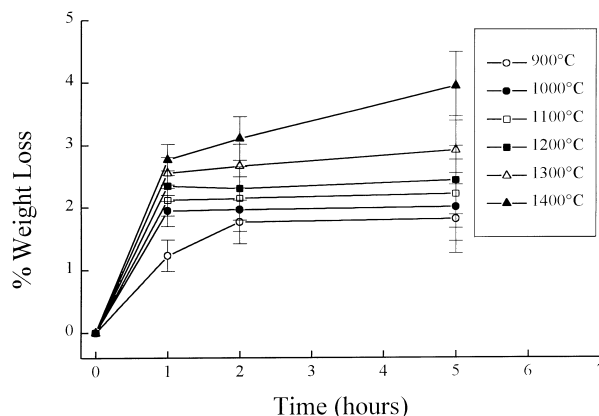| Sample	Na_2O	K_2O	Fe_2O_3	SiO_2	Residual H_2O
A	0.457	0.017	0.097	0.120	1–1.5
B	0.009	0.002	0.015	0.037	0
C	0.009	0.004	0.052	0.068	0

Fig. 2. Weight loss of alumina samples calcined 1, 2, and 5 h at 900, 1000, 1100, 1200, 1300, and 1400°C in reducing conditions under vacuum ($P = 10^{-4}$ atm).

the furnace was again reduced to below 10^{-4} atm, starting at this point the thermal treatment. In this case, the vacuum pump was operated throughout the process. Both at atmospheric pressure (N_2) and under vacuum, the graphite linning the furnace maintained low P_{O_2} throughout calcination by reaction with evolved O_2.

Samples were weighed before and after calcination. Chemical analyses were performed by ICP-AES in a Varian Liberty 200 spectrometer. Powder X-ray diffraction patterns were recorded in a Siemens D5000 diffractometer.

3. Results

The amorphous alumina used contained as its major impurity nearly 0.5% wt of Na_2O (Table 1). Calcination of this amorphous alumina at 1200°C in air promotes the crystallization of corundum and $Na_2O\cdot11Al_2O_3$. Weight loss of this material was about 1–1.5% wt due to evaporation of residual water.

3.1. Calcinations under vacuum (p = 10^{-4} atm)

As can be seen in Fig. 2, when amorphous alumina was calcined at low pressure under reducing conditions, weight losses of 1–3% occurs during the first hour. No further losses are detected at temperatures below 1300°C. For any given reaction time, weight loss increased with temperature. Removal of Na_2O began at about 1000°C, and was completed within 1 h at temperatures of 1200°C

or higher (Fig. 3). In keeping with these analytical results, X-ray diffractometry showed that increasing the treatment temperature progressively reduced the amount of $Na_2O\cdot11Al_2O_3$ present, until none was detected in samples treated at or above 1100°C (Fig. 4).

3.2. Calcinations in N_2 at 1 atm pressure

When reducing calcination was carried out in a nitrogen atmosphere, samples weight losses occurs during the first hour at all temperatures except 900°C (Fig. 5). Total removal of Na_2O required temperatures of at least 1100°C, but was again completed within 1 h at temperatures of 1200°C or higher (Fig. 6). At these latter temperatures, Na_2O removal was as efficient as in the calcinations carried out under vacuum, but removal of the minor impurities Fe_2O_3 and SiO_2 was less efficient (Table 1).

4. Discussion

The above results show that the procedure described successfully purifies Na_2O from corundum both in vacuum ($P = 10^{-4}$ atm) and in a nitrogen atmosphere (N_2, $P = 1$ atm). In all cases, purification is attributed to the relative stabilities of alumina and the oxide impurity
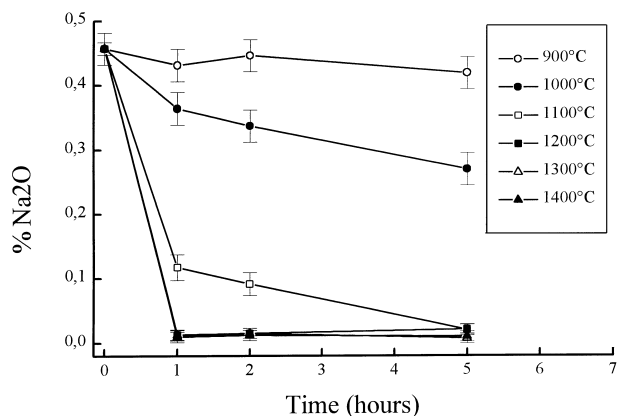
Fig, 3. Na$_2$O content (wt%) of alumina samples calcined 1, 2, and 5 h at 900, 1000, 1100, 1200, 1300, and 1400°C in reducing conditions under vacuum ($P = 10^{-4}$ atm).
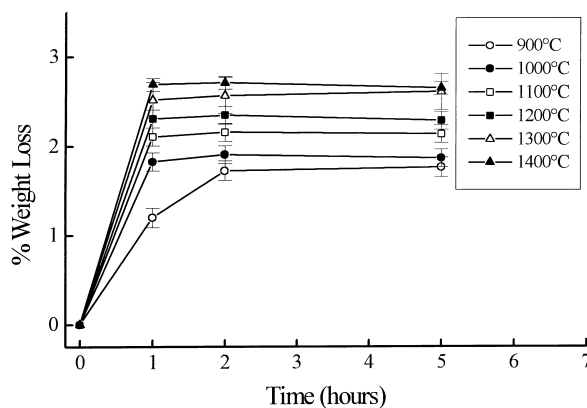

Fig. 5. Weight loss of alumina samples calcined at 900, 1000, 1100, 1200, 1300, and 1400°C in reducing conditions in N$_2$ at atmospheric pressure.
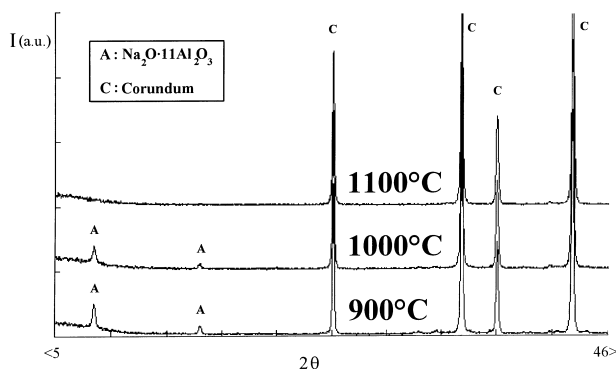

Fig. 4. Diffractograms of alumina samples calcined 1 h at 900, 1000, and 1100°C in reducing conditions under vacuum ($P = 10^{-4}$ atm).
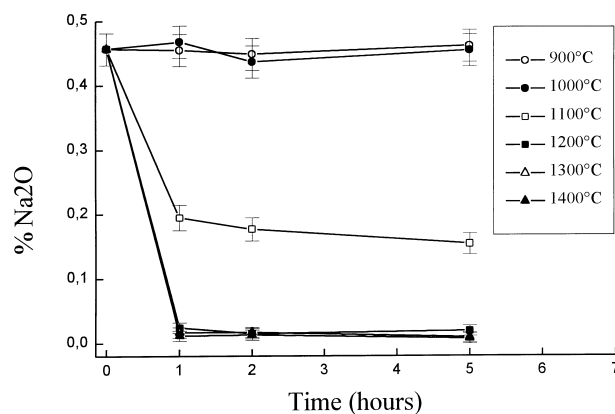

Fig. 6. Na$_2$O content (wt%) of alumina samples calcined at 900, 1000, 1100, 1200, 1300, and 1400°C in reducing conditions in N$_2$ at atmospheric pressure.

in reducing atmospheres at high temperature (Fig. 1). In particular, at high temperature and P_{O_2} in the appropriate range, alumina is stable but Na$_2$O undergoes the reaction

$$Na_2O \rightarrow 2Na + 1/2\ O_2$$

The experimental results show that at 10^{-4} atm this reaction requires temperatures greater than about 1000°C, and in N$_2$ at atmospheric pressure temperatures greater than about 1100°C. Since the boiling point of sodium is 882.9°C, its evaporation occurs immediately upon its formation. Exactly the same mechanism may be proposed for the removal of K$_2$O, the boiling point of potassium being 774°C. In the case of Fe$_2$O$_3$, the significant effect of lowering the operating pressure is due to removal of reduced iron taking place through evaporation, the vapour pressure of iron at 1300°C being only about 10^{-6} atm; while in the case of SiO$_2$ the reduction product, SiO, is gaseous.

The fact that at temperatures higher than 1200°C weight losses after 1 h were significantly greater than the

total impurity content of the amorphous alumina samples shows that part of the alumina must also have been reduced and volatilized. At temperatures of 1300°C or higher, reaction of the furnace lining with oxygen makes P_{O_2} fall below the threshold for reduction of alumina, and gaseous Al$_2$O is formed as the major product of this reduction reaction:[6–8]

$$Al_2O_3 \rightarrow Al_2O(g) + O_2(g)$$
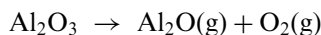
In the experiments carried out under vacuum, the evacuation of gaseous products by the vacuum pump will have promoted this reaction, and the higher the temperature the more intense this effect will have been (Fig. 2). In the experiments carried out in N$_2$ at atmospheric pressure, on the other hand, the accumulation of gaseous Al$_2$O will have halted the reduction of corundum (Fig. 5).

It may be noted that MgO and CaO are more stable than Al$_2$O$_3$ under the working conditions used. Thus this method of purification of corundum does not prevent

the use of minor quantities of MgO and CaO to control grain size during subsequent sintering.[9]

5. Conclusions

Impurities detracting from the end-product performance of corundum can be removed by high-temperature calcination in reducing atmospheres in a graphite-lined furnace. Under these conditions, reaction of oxygen with the furnace lining causes a fall in P_{O_2} to levels at which impurities are rapidly reduced to volatile species. Removal of impurities is enhanced by maintaining a pressure of 10^{-4} atm in the furnace. Application of this treatment to amorphous alumina or other aluminum oxides or hydroxides, such as gibbsite, yields high-purity corundum in a one-step process. Calcination of impure corundum in the same conditions yields high-purity corundum.

Acknowledgements

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