Sodium corrosion resistance of translucent alumina: effect of additives and sintering conditions

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The resistance of Al_2O_3 against corrosion by sodium in the temperature range 800 to 1000° C was studied by holding samples in liquid sodium in molybdenum containers for several hundred hours. Thermodynamic calculations indicating that Al_2O_3 is unstable in contact with sodium were confirmed by testing sapphire samples. A remarkable aspect was the large anisotropy in the corrosion resistance of sapphire. The effect of the sintering atmosphere and the amount of MgO and CaO dopant in polycrystalline alumina on the corrosion resistance was considered. Vacuum sintering yielded more resistant materials than hydrogen sintering. Low firing temperatures as well as low dopant levels also proved beneficial. In particular, the absence of CaO improves the corrosion resistance considerably. Consequently, the use of this additive should be avoided.

1. Introduction

Alumina is a common arc tube material for high-pressure sodium discharge lamps. Operating temperatures typically range from about 750° C at the ends of the tube to about 1250° C in the middle. Important properties are translucency, strength and chemical inertness. The addition of a few hundred ppm of dopant, usually MgO, is required for proper sintering to translucency. A further improvement in translucency can be obtained by adding an additional amount of CaO ([1], see also [2]) usually a few tenths wt ppm. It is known, however, that CaO segregates heavily on the grain boundaries of polycrystalline alumina [3]. This segregation possibly influences the corrosion of alumina by sodium. Furthermore, an influence of the sintering atmosphere on the corrosion resistance can be expected. A detailed picture of the corrosion phenomena is not yet available in spite of several investigations [4–6]. All these investigations were done with burning lamps. The conditions in these lamps are rather complicated, but the experiments do indicate that the addition of CaO has a detrimental influence. In order to obtain more insight, corrosion experiments were done on small alumina blocks encapsulated in a molybdenum box and heated in contact with sodium for several hundred hours at elevated temperature.
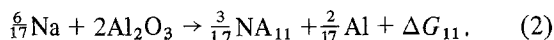
2. Sodium attack

When studying the stability of alumina in contact with sodium, inter-oxide compound formation should be taken into account. The following sodium-aluminates have been described in the literature [7, 8]:

$$N_5A, NA, NA_{5-7} \ (\beta''\text{-alumina}), NA_{9-11} \ (\beta\text{-alumina})$$

in which

$$N_xA_y = xNa_2O \cdot yAl_2O_3.$$

Thermodynamic data for NA and β-alumina are given in the literature[†]. These substances can be formed by reactions between liquid sodium or saturated sodium vapour and Al_2O_3 according to:

$$3Na + 2Al_2O_3 \rightarrow \tfrac{3}{2}NA + Al + \Delta G_1 \qquad (1)$$

$$\tfrac{6}{17}Na + 2Al_2O_3 \rightarrow \tfrac{3}{17}NA_{11} + \tfrac{2}{17}Al + \Delta G_{11}. \qquad (2)$$

TABLE I   Material characteristics

Material	Sintering	MgO (wt ppm)	CaO (wt ppm)	ρ (%)	D_{50} (μm)	$\ln\left(\dfrac{D_{50}}{D_{16}}\right)$
1	Vac, 1850° C − 8 h	100	2	99.94	19	0.52
2	Vac, 1850° C − 8 h	100	6	99.89	26	0.47
3	Vac, 1850° C − 8 h	100	16	99.91	13	0.55
4	Vac, 1850° C − 8 h	100	41	99.92	18	0.78
5	H_2, 1670° C − 8 h	100	2	99.71	11	0.37
6	H_2, 1670° C − 8 h	300	2	99.63	15	0.56
7	H_2, 1825° C − 8 h	100	2	99.65	5	0.99
8	H_2, 1825° C − 8 h	300	2	99.65	2	0.62

*Vac = vacuum 10^{-5} torr.
H_2 = moist H_2 (dewpoint ~ 15° C).
In all cases a holding time of 1 h at 1500° C precedes the final sintering step.
The theoretical density is assumed to be 3.986 g cm^{-3} [13].
For other symbols see text.

The free energy change[†], ΔG_1, is about − 3.3 and −2.7 kcal at 900 and 1000° C, respectively. For the second reaction, ΔG_{11} is approximately constant at −1.8 kcal. In principle, therefore, alumina is not stable in the presence of sodium.

3. Experimental techniques
3.1. Preparation and characterization
The materials were prepared using a commercially available starting powder[‡]. Details of the powder and preparation of the ceramics are given by de With [12]. Materials 1 to 4[§] were sintered in vacuum (10^{-5} torr) using the minimum amount of about 100 wt ppm MgO necessary to obtain a dense, translucent ceramic [13] meanwhile varying the CaO content. For materials 5 and 7 this minimum amount was used again but now sintered in moist hydrogen (dewpoint 15° C) at a relatively low and high temperature, respectively. Finally, materials 6 and 8 were also fired in hydrogen at these two temperatures, but now with the 300 wt ppm MgO. Further details are given in Table I.

After polishing and etching (see [12]) the area distribution of the grains was determined. From these data the volume grain size number distributions were calculated by means of the Saltikow–Johnson transformation [14]. The density was determined using Prokic's method [15].

3.2. Corrosion experiments
The kinetics of the reactions between alumina and sodium were studied by loading a molybdenum cup with alumina (either a block or an amount of powder) and an overdose of sodium. All samples were taken from the bulk of relatively large sintered blocks to avoid sinter skin-effects. The molybdenum was outgassed in a vacuum of about 10^{-5} torr for 1 h at 1000° C. The test samples (10 to 30 mm^3) were cleaned for 5 min at 50° C in diluted (1:1 vol parts) HNO_3, rinsed in demi-water, and dried in air. Before entering the molybdenum cup both the bulk pieces and the powders (grain size 45 to 90 μm) were fired in air for 1 h at 1000° C. After this pretreatment the sample was placed in the molybdenum cup, 20 to 50 mg sodium was added under argon atmosphere ($P_{O_2} \sim 10^{-3}$ torr) and the cup was sealed by welding. Heating to experimental conditions was performed in an electrically heated tube furnace, operating under a mixture of 75% N_2 and 25% H_2. The temperature of the cup was determined and controlled within 5° C. Experiments were performed at 900 and 1000° C. Holding times were 300 and 100 h, respectively. After the heat treatment the cup was opened in air, and the sample was immediately immersed in petroleum awaiting further sample preparation.

In the case of solid pieces, the test sample was cross-sectioned and polished under petroleum in order to avoid aqueous corrosion during preparation. The samples were examined for possible corrosion products in a scanning electron microscope (SEM) using energy dispersive analysis of X-rays (EDAX) and electron probe microanalysis (EPMA). The experiments with the powders were primarily meant to identify the reaction products

[†] All thermodynamic data were taken from references [9–11].
[‡] Ugine Kuhlman, A15Z.
[§] Throughout this paper the materials are indicated by their number in Table I.

using X-ray diffraction analyses. For comparison similar tests were also done on Verneuil-grown sappire.¶

4. Results and discussion: material characteristics

The material characteristics are given in Table I. It is clear that the density, ρ, is essentially constant and near to the theoretical density, although somewhat lower densities are obtained for materials 5 to 8, sintered in hydrogen. From previous experiments [12] with samples taken from the bulk of the material, it is known that no CaO and only 8% MgO is lost during vacuum sintering. For hydrogen sintering the loss is presumably less.

The mean grain size, D_{50}, ranges from 5 to 26 μm and thus is not constant. Furthermore the width of the distribution $\sigma = \ln(D_{50}/D_{16})$ is not constant either. Two more remarks can be made. First, it should be noted that the parameters D_{50} and σ only give an overall description of the grain-size distribution since some materials showed a tendency towards a bimodal distribution (see also [12]). Second, it would be a difficult if not impossible task to keep these parameters really constant while changing other parameters. In the interpretation of data, one should be aware of this fact.

Finally, we note that there is no agreement about the benefits of CaO addition on the translucency. Although the original patent [1] and de With [12] claim an increase in transmittance, Peelen [13] did not observe this effect.

5. Results and discussion: corrosion experiments

5.1. Sapphire

The intrinsic stability of alumina in the presence of sodium was studied using sapphire as test samples. Samples were exposed to the following experimental conditions: 800° C/500 h, 900° C/300 h and 1000° C/100 h, respectively in contact with sodium. Basal plane sections (indices 0 0 0 1) as well as prism-like sections (indices $1\bar{1}0\,0$) were investigated. The surfaces were polished, but sawn and fracture surfaces were also used for the prism-like planes.

The experiments clearly showed that alumina is indeed unstable in all three experimental conditions considered, as indicated by the thermodynamic calculations. The rate of the corrosion reaction, however, proved to be highly dependent upon crystal orientation at the surface and, of course, upon temperature. In all three conditions of temperature and time considered, the basal plane showed very little, if any, corrosion. In contrast, the prism-like planes clearly became corroded. At 800° C the corrosion was limited to the outer 5 μm after 500 h. With rising temperature, corrosion at this plane increased from about 150 μm in 300 h at 900° C to about 180 μm in 100 h at 1000° C. The sawn and fracture surfaces yielded very similar penetration depths. The results for the 1000° C/100 h treatment are shown in Fig. 1.

The X-ray diffraction diagram of sapphire powder heated for 10 h in contact with sodium only showed peaks that could be attributed to either α-alumina or NA. None of the peaks representative of other aluminates could be detected. That the reaction product is indeed NA, and NA only, was confirmed by line scans in the corroded areas using EPMA. No indication was found that the reaction product consisted of more than one phase, whereas the Al concentration in the corroded layer closely resembled that of NA, using alumina as a reference.

The large difference in corrosion rate noted between different crystal faces indicates that stability of alumina in the presence of pure sodium is a matter of kinetics rather than of thermodynamics. The fact, however, that the reaction proceeds in a given direction within the crystal, the reaction product being NA, proves that ΔG_1 is negative, as predicted by Equation 1. According to Equation 2, β-alumina could be formed thermodynamically, as well, but no indication was found that it actually did at these temperatures.

From these experiments it is concluded that in the temperature range considered, formation of NA at prism-like planes is the main corrosion phenomenon when single-crystalline alumina is brought into contact with sodium.

5.2. Translucent alumina: effect of CaO dope

A sample of material 1 (100 wt ppm MgO, 2 wt ppm CaO) was heated for 300 h at 900° C in contact with sodium (Fig. 2a), and the resulting corrosion was compared with that of sapphire after the same treatment (Fig. 1a). This polycrystalline sample did not show any detectable corrosion, whereas the prism-plane of the single crystal clearly became corroded in the same experimental

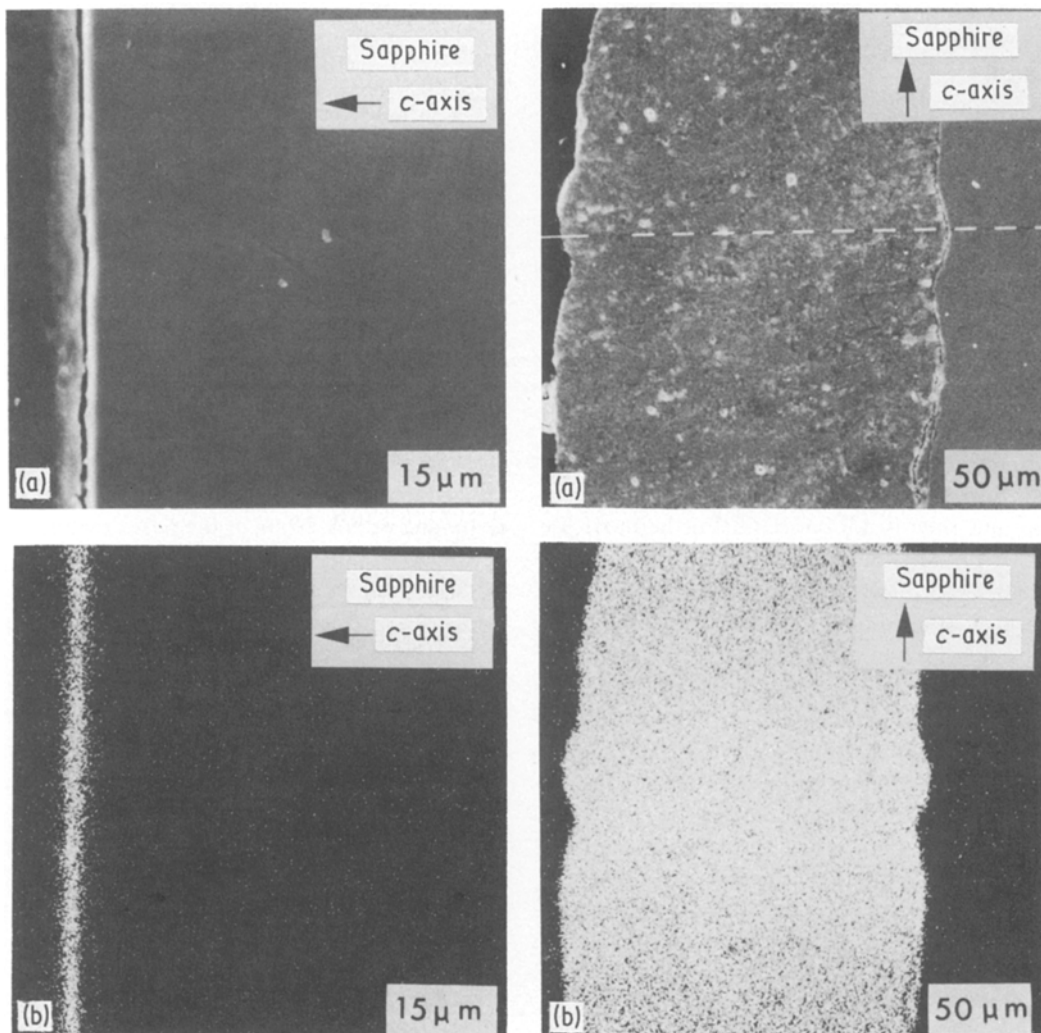¶ Industrie de Pierres Scientifiques Hrand Djevahirdjian S.A. CH-1870, Monthey, Switzerland.

Figure 1 Corrosion of a sapphire sample after 10 h at 1000° C. (a) Electron image (left ⊥ *c*-axis, right ∥ *c*-axis) (b) Na*K*α image (left ⊥ *c*-axis, right ∥ *c*-axis).

conditions. Apparently the corrosion resistance of this sintered sample is not adversely affected by the presence of grain boundaries, nor by the 100 wt ppm MgO added. Raising the temperature to 1000° C, however, resulted in extreme corrosion after 100 h (Fig. 2b). Within 100 h all sodium added (1 mol Na per mol Al_2O_3) did react with the sample, causing the outer part (∼0.5 mm) of the sample to disintegrate completely, the reaction product being NA. In fact the corrosion rate far exceeded that at the prism plane of sapphire after the same treatment. No indication was found that this accelerated corrosion was due to the presence of grain boundaries. Corrosion proceeded front-wise and no preferential corrosion along grain boundaries could be detected. These experi-

ments were repeated with a sample of material 2 differing from material 1 in its CaO content (6 wt ppm instead of 2). The results were analogous, indicating that such small amounts of CaO do not significantly affect the stability of the grain boundaries.

Raising the CaO content further to 16 wt ppm (material 3) resulted in serious corrosion after 300 h at 900° C in contact with sodium. Corrosion was clearly initiated at the grain boundaries. Sodium could be detected at the grain boundaries to a depth of at least 150 μm below the surface. Bulk corrosion was limited to the outer grain(s) (about 30 μm). Increasing the CaO content to 41 wt ppm resulted in even worse corrosion at 900° C. Grain-boundary corrosion extended at least to 1000 μm
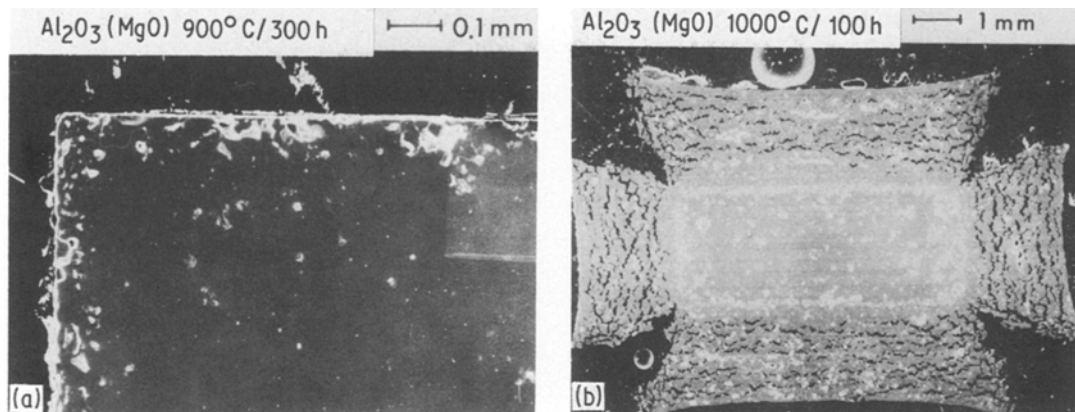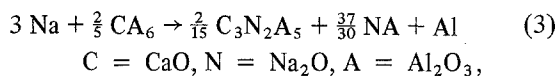
Figure 2 Corrosion of an alumina sample containing 100 wt ppm MgO and 2 wt ppm CaO (material 1) fired in vacuum ($\sim 10^{-5}$ torr): Electron images after (a) 300 h at 900° C, and (b) 100 h at 1000° C.

below the surface, whereas the outer $100\,\mu$m of the sample was completely converted into NA (Fig. 3). The excessive corrosion noted at 1000° C in the case of samples 1 and 2 was also found with samples 3 and 4.

From these experiments it can be concluded that segregation of CaO at grain boundaries seriously decreases the stability of these boundaries against penetration of sodium at 900° C. Although there is no conclusive evidence, the presence of CaO at the grain boundaries probably leads to the formation of $CaO \cdot 6Al_2O_3$ (CA_6). If it does, the resistance of the grain boundaries against penetration of sodium clearly depends upon the stability of this compound against attack by sodium.

From a thermodynamic point of view CA_6 is about as stable as Al_2O_3 itself. The free energy change for the reaction:

$$3\,\text{Na} + \tfrac{2}{5}\,CA_6 \rightarrow \tfrac{2}{15}\,C_3N_2A_5 + \tfrac{37}{30}\,NA + \text{Al} \qquad (3)$$
$$C = CaO, N = Na_2O, A = Al_2O_3,$$

at 800–1000° C is about -4.5 kcal, approximately equal to ΔG for Reaction 1. The presence of CA_6 at the grain boundaries evidently does not decrease the chemical stability of the alumina. There is, however, a large structural similarity between CA_6 and β-alumina. The high mobility of sodium ions in this latter material is well known. A more efficient initiation of Reaction 1 in the presence of CA_6 is thus conceivable.*

The fact that corrosion in the calcia-doped samples is not limited to the grain boundaries, but
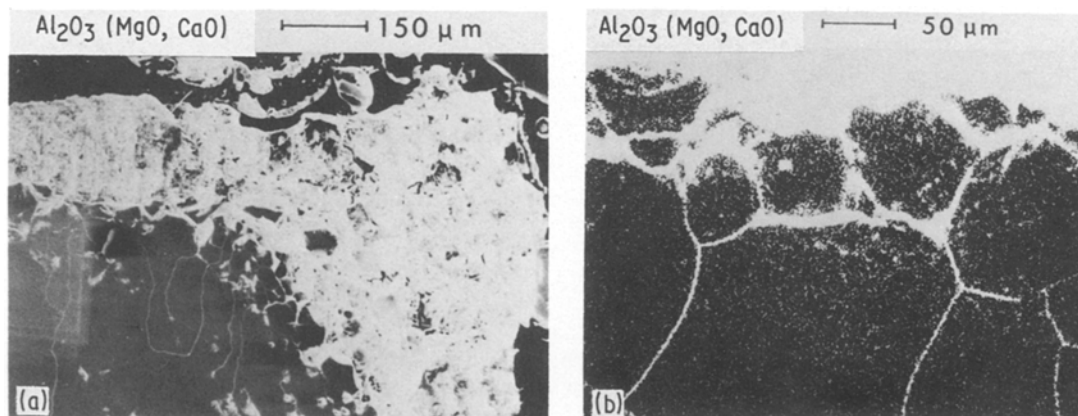

Figure 3 Corrosion of an alumina sample containing 100 wt ppm MgO and 42 wt ppm CaO (material 4) fired in vacuum ($\sim 10^{-5}$ torr) after 300 h at 900° C. (a) Electron image, (b) Na$K\alpha$ image.

*In fact, sodium corrosion experiments on CA_6 showed that the rate of attack is much larger than for Al_2O_3, although again preferentially the grain boundaries are attacked.
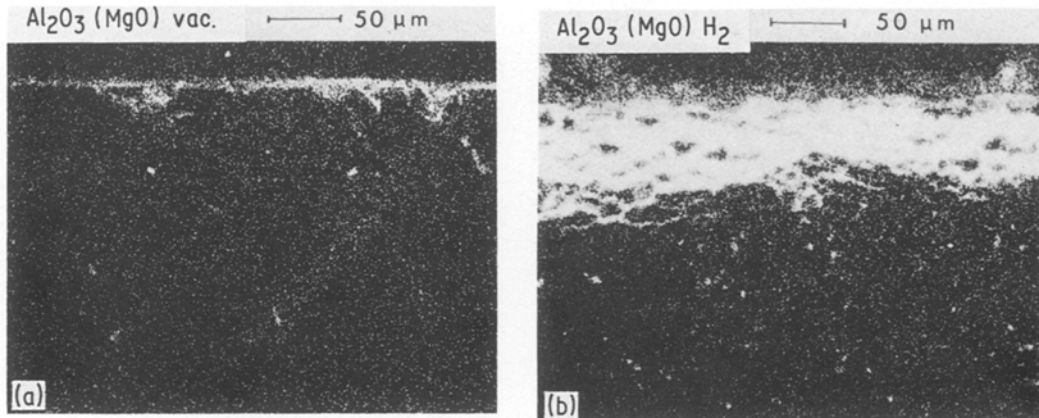
Figure 4 Corrosion of an alumina sample containing 100 wt ppm MgO and 2 wt ppm CaO after 300 h at 900° C (NaKα image). (a) Fired in vacuum ($\sim 10^5$ torr, material 1). (b) Fired in humid hydrogen ($T_{dew} \sim 15°$ C, material 5).

spreads out in the bulk of the grains, indicates that the apparent stability of the CaO-free materials at 900° C only results from problems in initiating the reaction in the absence of CaO (or other substances). The experiment at 1000° C using the same material indicates that at this temperature initiation is no longer a problem, and the presence of calcia is no longer a prerequisite for corrosion to occur. However, adding calcia still promotes corrosion at 1000° C because of more rapid diffusion of sodium along the grain boundaries.

From these experiments it is clear that the addition of CaO should be omitted in order to obtain optimal corrosion resistance.

5.3. Translucent alumina: effect of sintering conditions and MgO dope

To study the effect of sintering atmosphere on stability, the corrosion resistance of material 1 was compared with that of material 5 sintered from the same starting powder, again containing 100 wt ppm MgO, using the same sintering procedure except for the atmosphere, which was humid hydrogen instead of vacuum. This sample was again heated in contact with sodium for 300 h at 900° C (Fig. 4).

In contrast with the material sintered in vacuum, the hydrogen-sintered sample clearly became corroded. Although the material did not contain appreciable amounts of CaO, corrosion was again initiated at the grain boundaries. Sodium penetration along grain boundaries extended to at least 60 μm below the surface, whereas most grains in the outer layer of the sample corroded only par-

tially. Apparently, sintering in humid hydrogen leaves the grain boundaries in a more reactive state than sintering in vacuum. It should be noted, however, that the final MgO content of both samples after sintering might be somewhat different. Sintering in vacuum reduced the MgO content from 100 to 92 wt ppm [12] and this reduction is expected to be less in the case of humid hydrogen.

The effect of changing the MgO concentration was studied, keeping the CaO concentration as low as possible (~ 2 wt ppm). Four materials (5 to 8) were studied containing 100 (materials 5 and 6) and 300 (materials 7 and 8) wt ppm MgO, respectively, and using two sintering conditions, i.e. sintering at 1825° C (materials 5 and 7) and 1670° C (materials 6 and 8) both in humid hydrogen atmosphere.

All four examples were heated for 300 h at 900° C in contact with sodium. Materials 5 and 6 with the lower MgO content (~ 100 wt ppm) proved to be far more resistant than materials 7 and 8 with the higher MgO content (~ 300 wt ppm). In its turn, material 6 sintered at 1670° C proved to be more resistant than material 5 sintered at 1825° C, but still less resistant than the material sintered in vacuum at 1825° C, i.e. material 1. The 300 wt ppm MgO materials (materials 7 and 8) suffered from severe corrosion. The outer millimetre of these samples was converted almost completely into NA, and sodium pentrated the grain boundaries throughout the samples ($\sim 4 \times 4 \times 4$ mm³). All four samples considered clearly suffered from sodium penetration along grain boundaries.

These experiments show that, irrespective of sintering temperature, the corrosion resistance of H_2-sintered alumina drops drastically if the MgO content of the sinter powder is raised from 100 to 300 wt ppm. Furthermore, sintering at 1670° C resulted in at least as resistant materials as sintering at 1825° C.

6. Conclusion

On thermodynamic grounds it is predicted that Al_2O_3 is not stable in contact with sodium. This prediction has been confirmed by corrosion experts on sapphire and (polycrystalline) alumina at temperatures ranging from 800 to 1000° C. In this temperature regime, $Na_2O \cdot Al_2O_3$ was the only detectable corrosion product. Sapphire samples showed a large anisotropy in their corrosion resistance, the basal plane being considerably less attacked than the prism-like plane. This anisotropy plays a minor role in polycrystalline alumina because in that material grain-boundary penetration dominates. For polycrystalline alumina it is concluded from corrosion experiments on ceramics sintered in hydrogen that the addition of 100 wt ppm MgO results in more resistant materials than the addition of 300 wt ppm MgO. A slightly better relative corrosion resistance is obtained after sintering at 1670° C than after sintering at 1825° C. A much better corrosion resistance is obtained by firing in vacuum; in particular, grain-boundary penetration is significantly less. On the other hand, the addition of CaO, which is done to increase the optical transmittance, is detrimental to the corrosion resistance. Since it has been shown that CaO also has a harmful influence on the mechanical properties of alumina [12], the addition of CaO should be avoided.

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