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Reactions in the CaO–Cs₂O–Al₂O₃ System at 900°C

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Abstract

Reactions in the system CaO–Cs₂O–Al₂O₃ were investigated. On the basis of the experimental results, a compatibility diagram for this system at 900°C is proposed. In this system a new compound was found and formulated as Cs₂O 2CaO 4Al₂O₃. The X-ray diffraction pattern was measured and the cell parameters were derived.

The phase relation results can be used to draw some conclusions about the caesium compatibility of Al₂O₃ containing calcia. We found that all calcium aluminates react with Cs₂O forming a stable compound. From these results we conclude that calcium will have a negative effect on the caesium resistance of Al₂O₃.

1 Introduction

Only work on one quasi-ternary phase diagram involving Cs₂O and Al₂O₃ has been done in the past, namely on the Cs₂O–SiO₂–Al₂O₃ diagram. This was done because of its importance for the nuclear technology. Yet there are some other important applications which merit such an investigation. In our own laboratory, work is performed on thermionic energy converters. Thermal energy is converted into electric energy by electron emission from a high temperature electrode (emitter) to a low temperature electrode (collector). In order to avoid space charge effects caesium vapour is introduced in the interelectrode space. Caesium is chosen here because of its low ionization potential. For the same reason this element is used in closed-cycle magneto hydrodynamic generators. In both applications, materials are exposed to temperatures in the range of 1000–1700°C. Under these circumstances caesium is highly aggressive and only few materials have a sufficient corrosion resistance. A number of research studies have been carried out in the past with the objective of finding such materials. Alumina seems to be one of the best. The corrosion resistance is, however, largely determined by the sinter additives and grain boundary phases. For instance, silica additions have a detrimental effect. Other well known sintering aids for the densification of alumina are magnesia and calcia.
The studies reported so far were always performed by exposing a material for a certain amount of time to caesium vapour at a certain temperature, and examining it afterwards in order to find out whether the material had been damaged or not. In this study we want to present some results of a more fundamental approach, that is the phase diagram examination of the CaO-Cs2O-Al2O3 system. In the quasi-binary Cs2O-Al2O3 system, two compounds have been reported in the literature 13,14. Cs2O Al2O3 (CsA) was made by reacting CsNO3 with Al2O3 3H2O (Throughout this paper CaO--Ca, Al2O3 = A and Cs2O = Cs) CsA will react with water forming a hydrate CsA + 4H2O(CsA 4H2O) 15. Above 550°C this reaction will go in the opposite direction. The second phase mentioned in this system was CsA 11, which is formed by heating CsA for a year at 700°C. Because this phase is formed only after such a long reaction time and was never found in our experiments, it will not be taken into account in the present study.

The quasi-binary system CaO-Al2O3 has been the subject of numerous studies, mainly because of its importance to the cement industry. The two most recently published phase diagrams are very much alike (see Fig. 1) 16,17. The stability of CA6 at lower temperatures is a point of discussion. This phase is only formed at temperatures above ±1330°C,18 but does not dissociate at lower temperatures.19 Diffusion couple experiments of CaO against Al2O3 at 1330°C resulted in formation of all known calcium aluminates. The relative amounts of these phases in this diffusion couple were in the order C12A7 >> CA6 > CA5 > CA2 ≈ CA. Another study showed an increasing amount of CA6 at expense of CA and CA2 when going to higher temperatures.20 No studies of the phase diagram were reported at temperatures below 1000°C.

No information was found in the literature on the quasi-ternary system Cs2O-CaO-Al2O3 nor on the Cs2O-CaO system.

2 Experimental

The starting materials were Cs2CO3 (FO Optipur, >99.8%, E Merck AG, Darmstadt, FRG), CaCO3 (Zur Analyse, >99%, E Merck AG, Darmstadt, FRG) and Al2O3 (Extrapure, >99.995%, Les Rubis Synthetique des Alpes, Jarrie, France). Because Cs2CO3 is deliquescent, this material was handled in a glove box in order to be sure that no water was attracted. The powders were mixed in the appropriate amounts for the total weight to be about 2–5 g. These mixtures were pressed into 250–500 mg pellets and subsequently heated to 900°C in air in alumina crucibles (99.999%). During the heating, the contact between the pellet and crucible was minimized to two points. The crucibles were taken out of the furnace while still hot and transferred to the glove box to cool down. No visible corrosion of the crucibles took place during the experiments. Phases present in the pellet after this calcination procedure were identified by X-ray diffraction (XRD) using CuKα radiation. In order to prevent reaction between the phases and water vapour from ambient air during XRD, the diffractometer was evacuated.

The decomposition of CaCO3 and Cs2CO3 was measured using thermogravimetric analysis. This experiment shows that complete dissociation of the carbonates takes place between 650°C and 900°C. During calcination at 900°C, the Cs2O losses were often considerable. This means that the composition changed during the heat treatment. By measuring the weight before and after the heat treatment, however, we could calculate the resulting composition. The accuracy is good enough for our purpose, but one has to bear in mind that the real compositions might differ and must be checked afterwards.

2.1 A new quasi-ternary compound: Cs2O 2CaO 4Al2O3

In the first experiments (nos 1–3 in Fig. 2), we found from XRD measurements that together with Al2O3 and CsA an unknown compound was always formed. We developed a new method to locate this compound. The principle of this new method is based on the fact that CsA decomposes upon heating at 900°C, leaving pure Al2O3. So when we heat mixtures of CsA, Al2O3, and the unknown compound for long times, Cs2O will evaporate out of CsA until no CsA is present. When no Cs2O...
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evaporates from the unknown compound, the resulting compositions will lie on a straight line between Al₂O₃ and the unknown compound. Thermogravimetric analyses afterwards showed that indeed no Cs₂O evaporates from the unknown compound. Once the composition of the compound was roughly located, we heated mixtures 19-27 (see Fig 2) at 900°C until their weights had stabilized. The diffraction pattern of mixture 23 showed only peaks of the unknown, white compound. Chemical analyses of the sample resulted in a somewhat higher Cs₂O content than calculated (34.0 wt% Cs, 10.2 wt% Ca and 26.8 wt% Al). This corresponds best to Cs₂O 2CaO 4Al₂O₃ (CsC₂A₄). The diffraction pattern was measured more accurately using a Guinier camera (Johansson type—Enraf-Nomius BV, Delft, The Netherlands) and from these data the cell parameters were determined (see Table 1).

CsC₂A₄ was found to be monoclinic with lattice constants a = 8.2197 x 10⁻¹⁰ m, b = 5.2782 x 10⁻¹⁰ m, c = 7.7639 x 10⁻¹⁰ m, and axial angle β = 93.487°. The spacegroup probably P2₁/m.

Table 1. X-ray powder diffraction data of Cs₂O 2CaO 4Al₂O₃

<table>
<thead>
<tr>
<th>dₒ(10⁻¹⁰ m)</th>
<th>1/I₁</th>
<th>HKL</th>
<th>dₒ(10⁻¹⁰ m)</th>
<th>1/I₁</th>
<th>HKL</th>
<th>dₒ(10⁻¹⁰ m)</th>
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<tr>
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<td>1.898  2.5</td>
<td>320.222</td>
<td>1.899 1.1</td>
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<td>01</td>
<td>7.750</td>
<td>1.881  5.1</td>
<td>411  5.1</td>
<td>1.882 2.0</td>
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<tr>
<td>2.41  1.1</td>
<td>14</td>
<td>5.470</td>
<td>1.856  7.1</td>
<td>31  2.0</td>
<td>1.862 3.1</td>
<td></td>
</tr>
<tr>
<td>2.34  5.1</td>
<td>35</td>
<td>4.339</td>
<td>1.818  8.1</td>
<td>314.313</td>
<td>1.819 5.1</td>
<td></td>
</tr>
</tbody>
</table>

The crystal system is monoclinic with lattice constants a = 8.2197 x 10⁻¹⁰ m, b = 5.2782 x 10⁻¹⁰ m, c = 7.7639 x 10⁻¹⁰ m, and axial angle β = 93.487°.
2.2 Compatibility diagram

The experiments discussed so far, produced information about the Cs₂O-rich part of the compatibility diagram. In order to get information about the CaO–Al₂O₃–Cs₂C₂A₄ triangle, we set up another type of experiment. All the known calcium aluminates were synthesized in pure form by high temperature syntheses. Samples of these compounds were placed in an alumina crucible also containing Cs₂CO₃ and heated for 60 h at a temperature of 900°C. CsA, C₁₂A₇, and CA react with a large excess Cs₂O (50% Cs₂O in overall composition) forming CaO and Cs₂C₂A₄. When CA₂, on the other hand, reacts with a large excess Cs₂O, Cs₂C₂A₄ is the only phase detected by XRD. The reactions of the calcium aluminates with smaller amounts Cs₂O can be written as

\[ \text{C₃A + 1\% Cs₂O} \rightarrow \text{CaO + C₃A + Cs₂C₂A₄} \]
\[ \text{C₁₂A₇ + 1\% Cs₂O} \rightarrow \text{Cs₂C₂A₄ + C₁₂A₇ + Ca} \]
\[ \text{CA + 5\% Cs₂O} \rightarrow \text{Cs₂C₂A₄ + C₁₂A₇ + CA} \]
\[ \text{CA₂ + 5\% Cs₂O} \rightarrow \text{CA₂ + Cs₂C₂A₄} \]

All the results are in good agreement with the diagram proposed by us in Fig 4. The dashed lines between CsA and Cs₂C₂A₄ are used to indicate that, although CsA is not stable at 900°C, CsA and Cs₂C₂A₄ were found together at the beginning of the experiments. Cs₂O will evaporate out of CsA when

Thermogravimetric analysis showed no weight loss up to 1130°C (see Fig 3). At this temperature Cs₂O starts to evaporate very slowly until no Cs₂O is present at 1500°C. When Cs₂C₂A₄ is left in humid air, it picks up water and loses the crystallinity at the same time.

Fig. 2. Representation of some illustrative experiments (●). Starting compositions (CsCO₃–CaCO₃–Al₂O₃ mixtures), (○) Cs₂O Al₂O₃, Al₂O₃, and Cs₂O 2CaO 4Al₂O₃ (samples heated 20 h, weights had not stabilized yet), (●) CaO and Cs₂O 2CaO 4Al₂O₃ (samples heated 20 h, weights had not stabilized yet), (x) pure Cs₂O 2CaO 4Al₂O₃. One should bear in mind that the end compositions are calculated and could differ a little from reality.

Fig. 3. Thermogravimetric plot of Cs₂O 2CaO 4Al₂O₃. Heating rate is 5°C/min. Sample is heated from 20 to 850°C and held for 10 h at that temperature. Then it is heated to 900°C, held for 10 h, etc. The marks are the weights after 10 h at that temperature.

Fig. 4. Compatibility diagram at 900°C in the Cs₂O–CaO–Al₂O₃ system. The shaded area is not filled in because it is not completely clarified.
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3 Discussion

All the experimental results we obtained during this study are in good agreement with the compatibility diagram proposed by us. In spite of this, we should also make some critical remarks.

In the Al₂O₃-rich part of the diagram, two compounds are reported in literature which we did not find during our own investigations. Only once has it been reported that CsAl₁₁ can be formed after a year heating at 700°C and that this compound is stable up to 1050°C. We decided to leave it out of the diagram for the reasons that the compound was only reported once and because it was never found during our own investigations.

The problem with CA₆ is well known. It is not formed at 900°C but it is believed to be stable at that temperature. It is known that CaO segregates on the grain boundaries of polycrystalline Al₂O₃ (Ref. 21) probably leading to the formation of CA₆. This is the reason why it is important to know the behaviour of this compound when it is exposed to Cs₂O. For this reason, we did not want to leave CA₆ out of the diagram, although we do not know the exact phase relations.

As mentioned above, CaO segregates to the grain boundaries of Al₂O₃. As shown in the experiments, all the calcium alumnates react with Cs₂O to form CsC₂A₄. This means that even without knowing in which form (phase) CaO is present on the grain boundaries, we can predict from the diagram proposed by us that the grain boundaries will be corroded by Cs₂O. From these results, one may conclude that it is better to avoid CaO as a sinter aid for alumina that is to be used in Cs containing atmospheres.

Acknowledgment

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