

# Reactions in the CaO–Cs<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub> System at 900°C

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## Abstract

Reactions in the system CaO–Cs<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub> 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 Cs<sub>2</sub>O·2CaO·4Al<sub>2</sub>O<sub>3</sub>. 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 Al<sub>2</sub>O<sub>3</sub> containing calcia. We found that all calcium aluminates react with Cs<sub>2</sub>O forming a stable compound. From these results we conclude that calcium will have a negative effect on the caesium resistance of Al<sub>2</sub>O<sub>3</sub>.

Es wurden die Reaktionen im System CaO–Cs<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub> untersucht. Anhand der experimentellen Ergebnisse wurde ein Kompatibilitätsdiagramm bei 900°C aufgestellt. In diesem System wurde eine neue Phase gefunden, der die Formel Cs<sub>2</sub>O·2CaO·4Al<sub>2</sub>O<sub>3</sub> zugeordnet wurde. Mittels Röntgenbeugungsdiagrammen wurden die Parameter der Elementarzelle bestimmt.

Aufgrund der Ergebnisse können Aussagen über den Einfluß von Cs auf CaO-haltiges Al<sub>2</sub>O<sub>3</sub> gemacht werden. Wir fanden heraus, daß alle Kalziumaluminat mit Cs<sub>2</sub>O unter Bildung einer stabilen Verbindung reagieren. Daraus schließen wir, daß Kalzium einen negativen Einfluß auf den Cs-Widerstand von Al<sub>2</sub>O<sub>3</sub> hat.

On a étudié les réactions dans le système CaO–Cs<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>. On propose, pour ce système à 900°C, un schéma de compatibilité basé sur des résultats expérimentaux. On a trouvé dans ce système un composé nouveau de formule Cs<sub>2</sub>O·2CaO·4Al<sub>2</sub>O<sub>3</sub>. Ses paramètres de maille ont été obtenus par diffraction X.

Les données sur les relations de phases permettent

de tirer des conclusions sur le comportement vis-à-vis du césium d'une alumine contenant de la chaux. Nous avons trouvé que tous les aluminates de calcium réagissent avec Cs<sub>2</sub>O en formant un composé stable. Nous en déduisons que le calcium a un effet négatif sur la résistance au césium de l'alumine.

## 1 Introduction

Only work on one quasi-ternary phase diagram involving Cs<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> has been done in the past, namely on the Cs<sub>2</sub>O–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> diagram<sup>1,2</sup>. 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<sup>3–5</sup>. 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<sup>6–9</sup>. 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<sup>10–12</sup>. 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  $\text{CaO}-\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$  system. In the quasi-binary  $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$  system, two compounds have been reported in the literature<sup>13,14</sup>  $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3$  (CsA) was made by reacting  $\text{CsNO}_3$  with  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (Throughout this paper  $\text{CaO} = \text{C}$ ,  $\text{Al}_2\text{O}_3 = \text{A}$  and  $\text{Cs}_2\text{O} = \text{Cs}$ ) CsA will react with water forming a hydrate  $\text{CsA} + 4\text{H}_2\text{O} \rightarrow \text{CsA} \cdot 4\text{H}_2\text{O}$ <sup>15</sup> Above  $550^\circ\text{C}$  this reaction will go in the opposite direction. The second phase mentioned in this system was  $\text{CsA}_{11}$ , which is formed by heating CsA for a year at  $700^\circ\text{C}$ . 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  $\text{CaO}-\text{Al}_2\text{O}_3$  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)<sup>16,17</sup> The stability of  $\text{CA}_6$  at lower temperatures is a point of discussion. This phase is only formed at temperatures above  $\pm 1330^\circ\text{C}$ ,<sup>18</sup> but does not dissociate at lower temperatures.<sup>19</sup> Diffusion couple experiments of  $\text{CaO}$  against  $\text{Al}_2\text{O}_3$  at  $1330^\circ\text{C}$  resulted in formation of all known calcium aluminates. The relative amounts of these phases in this diffusion couple were in the order  $\text{C}_{12}\text{A}_7 \gg \text{C}_3\text{A} > \text{CA}_6 > \text{CA}_2 \cong \text{CA}$ . Another study showed an increasing amount of  $\text{CA}_6$  at expense of  $\text{CA}$  and  $\text{CA}_2$  when going to higher temperatures.<sup>20</sup> No studies of the phase diagram were reported at temperatures below  $1000^\circ\text{C}$ .

No information was found in the literature on the

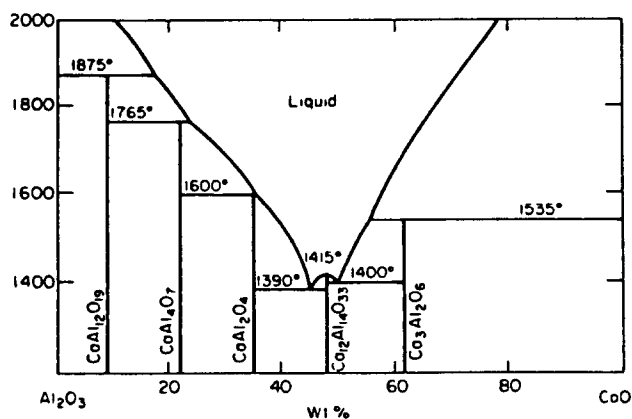


Fig. 1. The  $\text{CaO}-\text{Al}_2\text{O}_3$  system according to A. K. Chatterjee and G. I. Zhmoldin<sup>17</sup>

quasi-ternary system  $\text{Cs}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3$  nor on the  $\text{Cs}_2\text{O}-\text{CaO}$  system

## 2 Experimental

The starting materials were  $\text{Cs}_2\text{CO}_3$  (FO Optipur, >99.8%, E Merck AG, Darmstadt, FRG),  $\text{CaCO}_3$  (Zur Analyse, >99%, E Merck AG, Darmstadt, FRG) and  $\text{Al}_2\text{O}_3$  (Extrapure, >99.995%, Les Rubis Synthetique des Alpes, Jarrie, France). Because  $\text{Cs}_2\text{CO}_3$  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  $900^\circ\text{C}$  in air in alumina crucibles (99.99%) for 24 up to 200 h. 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  $\text{CuK}\alpha$  radiation. In order to prevent reaction between the phases and water vapour from ambient air during XRD, the diffractometer was evacuated.

The decomposition of  $\text{CaCO}_3$  and  $\text{Cs}_2\text{CO}_3$  was measured using thermogravimetric analysis. This experiment shows that complete dissociation of the carbonates takes place between  $650^\circ\text{C}$  and  $900^\circ\text{C}$ .

During calcination at  $900^\circ\text{C}$ , the  $\text{Cs}_2\text{O}$  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: $\text{Cs}_2\text{O} \cdot 2\text{CaO} \cdot 4\text{Al}_2\text{O}_3$

In the first experiments (nos 1–3 in Fig. 2), we found from XRD measurements that together with  $\text{Al}_2\text{O}_3$  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  $900^\circ\text{C}$ , leaving pure  $\text{Al}_2\text{O}_3$ . So when we heat mixtures of CsA,  $\text{Al}_2\text{O}_3$ , and the unknown compound for long times,  $\text{Cs}_2\text{O}$  will evaporate out of CsA until no CsA is present. When no  $\text{Cs}_2\text{O}$

evaporates from the unknown compound, the resulting compositions will lie on a straight line between Al<sub>2</sub>O<sub>3</sub> and the unknown compound. Thermogravimetric analyses afterwards showed that indeed no Cs<sub>2</sub>O 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 Cs<sub>2</sub>O content than calculated (34.0 wt% Cs, 10.2 wt% Ca and 28.6 wt% Al). This corresponds best to Cs<sub>2</sub>O·2CaO·4Al<sub>2</sub>O<sub>3</sub> (CsC<sub>2</sub>A<sub>4</sub>). The diffraction pattern was measured more accurately using a Guinier camera (Johansson type—Enraf-Nonius BV, Delft, The Netherlands) and from these data the cell parameters were determined (see Table 1). CsC<sub>2</sub>A<sub>4</sub> was found to be monoclinic with lattice constants  $a = 8.2197 \times 10^{-10}$  m,  $b = 5.2782 \times 10^{-10}$  m,  $c = 7.7639 \times 10^{-10}$  m, axial angle  $\beta = 93.487^\circ$  and the spacegroup probably P2<sub>1</sub> or P2<sub>1/m</sub>.

Table 1. X-ray powder diffraction data of Cs<sub>2</sub>O·2CaO·4Al<sub>2</sub>O<sub>3</sub>

$d_{obs} (10^{-10} \text{ m})^a$	$I/I_1^b$	HKL <sup>c</sup>	$d_{calc} (10^{-10} \text{ m})^d$	$d_{obs} (10^{-10} \text{ m})$	$I/I_1$	HKL	$d_{calc} (10^{-10} \text{ m})$
8.204	1.3	100	8.205	1.8985	2.5	320, 222	1.8991
7.747	20	001	7.750	1.8811	5	41 $\bar{1}$	1.8812
5.476	14	101	5.470	1.8618	8	32 $\bar{1}$	1.8628
4.438	35	110	4.439	1.8186	6	014, 31 $\bar{3}$	1.8189
4.362	20	011	4.363	1.7963	2.0	11 $\bar{4}$	1.7974
4.103	8	200	4.102	1.7841	8	123	1.7845
3.908	50	11 $\bar{1}$	3.908	1.7689	1.0	402	1.7689
3.875	35	002	3.875	1.7541	3	41 $\bar{2}$ , 114	1.7545
3.803	2.5	111	3.798	1.7336	2.5	32 $\bar{2}$	1.7345
3.723	14	20 $\bar{1}$	3.720	1.7232	6	313	1.7234
3.588	5	10 $\bar{2}$	3.589	1.7205	6	130	1.7203
3.4251	45	102	3.4242	1.7117	8	22 $\bar{3}$ , 204	1.7118
3.2391	50	210	3.2390	1.6838	6	13 $\bar{1}$	1.6840
3.1216	25	012	3.1235	1.6754	1.6	131	1.6749
3.0404	45	21 $\bar{1}$	3.0409	1.6562	2.0	40 $\bar{3}$ , 223	1.6574
2.9678	70	112	2.9679	1.6192	12	420	1.6195
2.9391	50	211	2.9387	1.6168	12	230	1.6170
2.9063	8	20 $\bar{2}$	2.9065	1.6012	6	42 $\bar{1}$ , 032	1.6014
2.8728	14	112	2.8726	1.5901	6	23 $\bar{1}$	1.5905
2.7349	6	202, 300	2.7350	1.5797	8	13 $\bar{2}$ , 41 $\bar{3}$	1.5800
2.6396	100	020	2.6391	1.5753	10	231	1.5753
2.5311	3	301	2.5311	1.5670	2.0	510	1.5669
2.5113	10	120	2.5123	1.5617	2.5	024, 32 $\bar{3}$ +	1.5618
2.4981	25	021	2.4982	1.5565	4	31 $\bar{4}$	1.5559
2.4233	8	103	2.4221	1.5484	3	12 $\bar{4}$	1.5482
2.3773	8	121	2.3769	1.5401	1.0	10 $\bar{5}$	1.5401
2.3200	12	013	2.3202	1.5206	2.0	124, 42 $\bar{2}$	1.5205
2.2819	1.3	311	2.2823	1.4842	2.5	22 $\bar{4}$	1.4839
2.2651	5	11 $\bar{3}$	2.2653	1.4789	5	502, 11 $\bar{5}$ +	1.4788
2.2489	6	20 $\bar{3}$	2.2484	1.4694	1.6	422	1.4693
2.2195	12	220	2.2195	1.4540	2.5	033, 40 $\bar{4}$	1.4537
2.2003	2.0	113	2.2014	1.4485	4	115	1.4485
2.1811	20	022	2.1812	1.4405	3	13 $\bar{3}$	1.4403
2.1519	2.5	22 $\bar{1}$	2.1525	1.4244	2.5	512, 50 $\bar{3}$ +	1.4245
2.1282	1.0	203	2.1283	1.3676	2.0	404, 600+	1.3675
2.0902	12	122	2.0903	1.3403	2.0	31 $\bar{5}$	1.3397
2.0683	2.5	21 $\bar{3}$	2.0686	1.3305	2.5	12 $\bar{5}$	1.3302
2.0511	8	400	2.0511	1.3248	2.0	43 $\bar{1}$	1.3248
2.0093	2.5	312	2.0093	1.3200	4	040	1.3196
1.9737	2.5	213	1.9739	1.3014	4	041	1.3008
1.9537	8	401, 22 $\bar{2}$	1.9538	1.2910	2.0	22 $\bar{5}$ , 50 $\bar{4}$ +	1.2912
1.9370	10	004, 30 $\bar{3}$	1.9376	1.2785	3	134, 43 $\bar{2}$	1.2783
1.9117	6	104, 410	1.9118	1.2660	2.0	333, 602	1.2658

The crystal system is monoclinic with lattice constants  $a = 8.2197 \times 10^{-10}$  m,  $b = 5.2782 \times 10^{-10}$  m,  $c = 7.7639 \times 10^{-10}$  m, and axial angle  $\beta = 93.487^\circ$ .

<sup>a</sup>  $d_{obs}$  is the observed crystal spacing

<sup>b</sup>  $I/I_1$  is the normalized observed intensity

<sup>c</sup> HKL are the Miller indices

<sup>d</sup>  $d_{calc}$  is the calculated crystal spacing

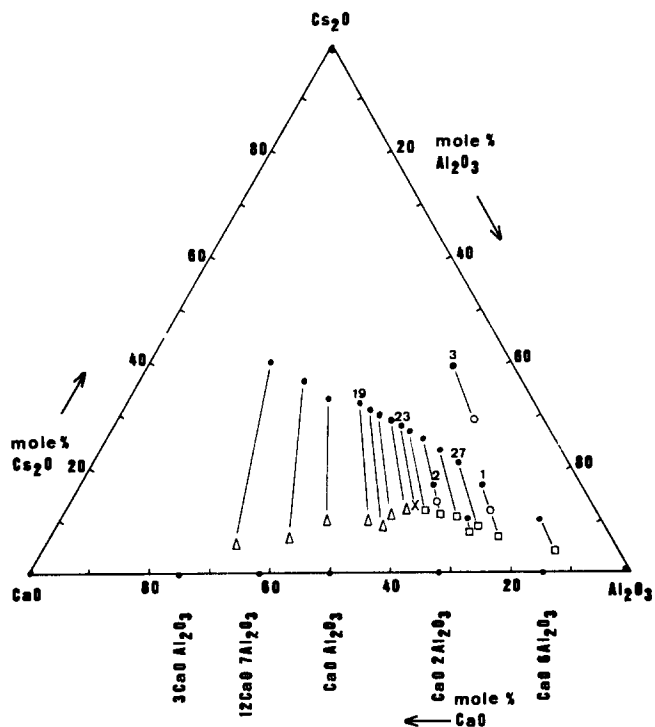


Fig. 2. Representation of some illustrative experiments (●) Starting compositions (CsCO<sub>3</sub>-CaCO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> mixtures), (○) Cs<sub>2</sub>O Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Cs<sub>2</sub>O 2CaO 4Al<sub>2</sub>O<sub>3</sub> (samples heated 20h, weights had not stabilized yet), (△) CaO and Cs<sub>2</sub>O 2CaO 4Al<sub>2</sub>O<sub>3</sub>, (□) Al<sub>2</sub>O<sub>3</sub> and Cs<sub>2</sub>O 2CaO 4Al<sub>2</sub>O<sub>3</sub>, (×) pure Cs<sub>2</sub>O 2CaO 4Al<sub>2</sub>O<sub>3</sub>. One should bear in mind that the end compositions are calculated and could differ a little from reality

Thermogravimetric analysis showed no weight loss up to 1130°C (see Fig 3) At this temperature Cs<sub>2</sub>O starts to evaporate very slowly until no Cs<sub>2</sub>O is present at 1500°C When CsC<sub>2</sub>A<sub>4</sub> is left in humid air, it picks up water and loses the crystallinity at the same time

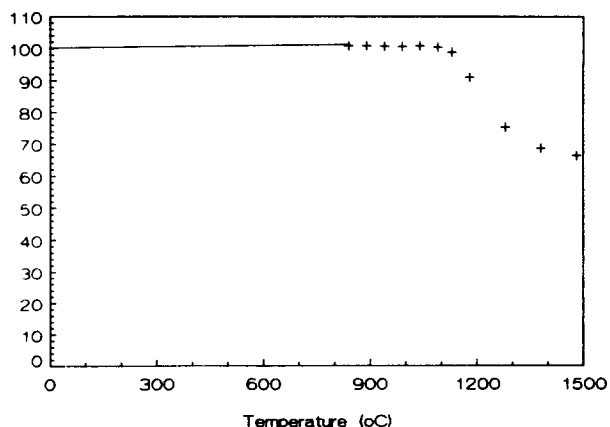
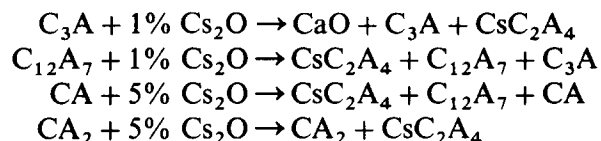


Fig. 3. Thermogravimetric plot of Cs<sub>2</sub>O 2CaO 4Al<sub>2</sub>O<sub>3</sub>. Heating rate is 5°C/min. Sample is heated from 20 to 850°C and held for 10 h at that temperature. Then it is heated to 900°C, held for 10h, etc. The marks are the weights after 10h at that temperature

### 2.2 Compatibility diagram

The experiments discussed so far, produced information about the Cs<sub>2</sub>O-rich part of the compatibility diagram. In order to get information about the CaO-Al<sub>2</sub>O<sub>3</sub>-CsC<sub>2</sub>A<sub>4</sub> 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 Cs<sub>2</sub>CO<sub>3</sub> and heated for 60 h at a temperature of 900°C. C<sub>3</sub>A, C<sub>12</sub>A<sub>7</sub> and CA react with a large excess Cs<sub>2</sub>O (50% Cs<sub>2</sub>O in overall composition) forming CaO and CsC<sub>2</sub>A<sub>4</sub>. When CA<sub>2</sub>, on the other hand, reacts with a large excess Cs<sub>2</sub>O, CsC<sub>2</sub>A<sub>4</sub> is the only phase detected by XRD. The reactions of the calcium aluminates with smaller amounts Cs<sub>2</sub>O can be written as



All the results are in good agreement with the diagram proposed by us in Fig 4. The dashed lines between CsA and CsC<sub>2</sub>A<sub>4</sub> are used to indicate that, although CsA is not stable at 900°C, CsA and CsC<sub>2</sub>A<sub>4</sub> were found together at the beginning of the experiments. Cs<sub>2</sub>O will evaporate out of CsA when

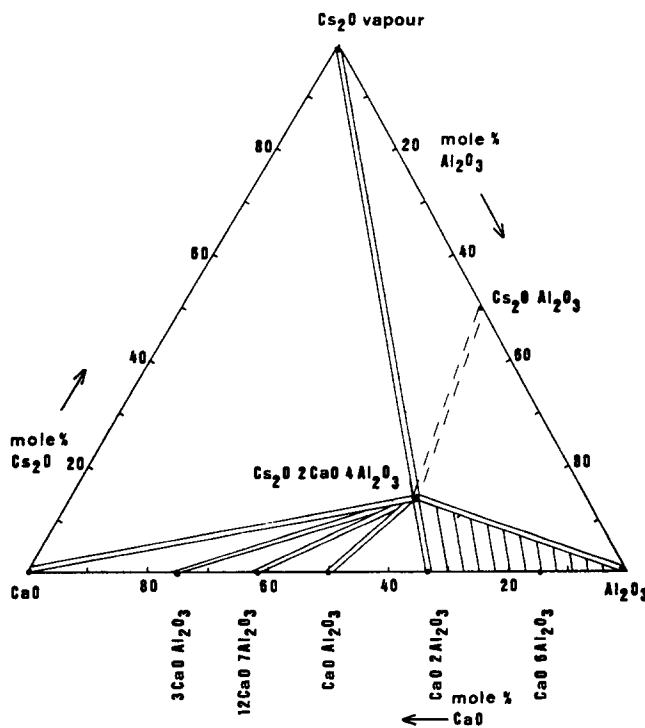


Fig. 4. Compatibility diagram at 900°C in the Cs<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub> system. The shaded area is not filled in because it is not completely clarified

heated for longer times in an open system, leaving Al<sub>2</sub>O<sub>3</sub> and evaporated Cs<sub>2</sub>O

In the Al<sub>2</sub>O<sub>3</sub>-rich part of the diagram, some problems arose. The results of the CA<sub>6</sub> + Cs<sub>2</sub>CO<sub>3</sub> experiment could not be understood on the basis of the compatibility diagram we constructed. When CA<sub>6</sub> was heated together with Cs<sub>2</sub>CO<sub>3</sub>, we found that an amorphous material had been formed. This experiment neither confirms nor contradicts the proposed diagram. In order to verify the stability of CA<sub>6</sub>, this compound was heated for 1000 h at 900°C. No signs of decomposition were found. On the other hand CA<sub>6</sub> could not be formed within 1000 h at 900°C out of a CaCO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> mixture. Thus, no conclusion about the stability of CA<sub>6</sub> at 900°C could be drawn from these experiments. This part of the diagram is not completely understood and should therefore be studied more closely.

### 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 Al<sub>2</sub>O<sub>3</sub>-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 CsA<sub>11</sub> 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 CA<sub>6</sub> 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 Al<sub>2</sub>O<sub>3</sub> (Ref. 21) probably leading to the formation of CA<sub>6</sub>. This is the reason why it is important to know the behaviour of this compound when it is exposed to Cs<sub>2</sub>O. For this reason we did not want to leave CA<sub>6</sub> out of the diagram, although we do not know the exact phase relations.

As mentioned above, CaO segregates to the grain boundaries of Al<sub>2</sub>O<sub>3</sub>. As shown in the experiments, all the calcium aluminates react with Cs<sub>2</sub>O to form Cs<sub>2</sub>A<sub>4</sub>. 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 Cs<sub>2</sub>O. 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.

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### References

- Odoj, R. & Hilpert, K., Mass spectrometric study of the evaporation of crystalline compounds in the cesium oxide–aluminum oxide–silicon oxide Cs<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system. 1. The synthetic compound cesium aluminosilicate (CsAlSi<sub>2</sub>O<sub>6</sub>) and the mineral pollucite. *High Temp–High Pressures*, **12** (1980) 93–8.
- Solov'eva, T. V., Moroz, I. Kh. & Vydrík, G. A., X-ray diffraction study of the synthesis of aluminum cesium disilicate. *Russ J Inorg Chem*, **15** (1970) 909–11.
- Wolff, L. R., Heinen, C. J. & van de Wouw, G. P., Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>–Mo as a thermionic emitter material. *High Temp–High Pressures*, **13** (1981) 69–77.
- Gubbels, G. H. M., Wolff, L. R. & Metselaar, R., Electron emission microscope measurements on cermet electrodes for thermionic converters. *Solid State Ionics*, **16** (1985) 47–54.
- Gubbels, G. H. M., Wolff, L. R. & Metselaar, R., A thermionic energy converter with polycrystalline molybdenum electrodes. *J Appl Phys*, **64**(3) (1988) 1508–12.
- Wagner, P. & Coriell, S. R., High-temperature compatibility of cesium gas with some dielectrics. *Rev Sci Instr*, **30** (1959) 937–8.
- Shivka, M. J., A study of cesium vapor attack on thermionic converter construction materials. *Advanced Energy Conversion*, **3** (1963) 157–65.
- Hargreaves, F., Mayo, G. T. J. & Thomas, A. G., A study of the long-term compatibility of thermionic converter materials with caesium. *J of Nucl Mater*, **18** (1966) 212–18.
- Britt, E. J., Desplat, J. L., Gulden, T., Chin, J. & Cone, V., Long-life insulators for in-core thermionics. In *Proceedings of the 20th Intersociety Energy Conversion Engineering Conference*. Society of Automotive Engineers, Inc., 400 Commonwealth Drive, Warrendale, PA 15096, 1985, pp. 3 499–3 512.
- Smith, R. G., Hargreaves, F., Mayo, G. T. J. & Thomas, A. G., The compatibility of thermionic converter materials with cesium. *J Nucl Mater*, **10** (1963) 191–200.
- Higgins, J. K., Reaction of alumina with cesium vapor. *Trans Brit Ceram Soc*, **65** (1966) 643–59.
- Grossman, L. N., Interactions in the system Cs<sub>18</sub>–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>. *Rev Int hautes Temper Refract*, **16** (1979) 255–61.
- Langlet, G., Centre d'Etudes Nucleaires de Saclay. Rapport CEA-R-3853, 1969.
- Semenov, N. N., Merkulov, A. G. & Vorsina, I. A., The synthesis and study of the compounds of the Cs<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub> system. *Ser Khim Nauk*, **1**(2) (1967) 75–83.
- Barkova, F. F., Pysina, N. E. & Strukulenko, N. A., Rare alkali elements. Sb Dokl naII Vsesojuznom Sov. Novosibirsk Nauka 1967.
- Nurse, R. W., Welch, J. H. & Majumdar, A. J., The CaO–Al<sub>2</sub>O<sub>3</sub> system in a moisture-free atmosphere. *Trans Brit Ceram Soc*, **64** (1965) 409–17.
- Chatterjee, A. K. & Zhmoidin, G. I., The phase equilibrium diagram of the system CaO–Al<sub>2</sub>O<sub>3</sub>–CaF<sub>2</sub>. *J Mater Sci*, **7** (1972) 93–7.

- 18 Kohatsu, I & Brindley, G W, Solid state reactions between CaO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> *Z Phys Chem*, **60** (1968) 79–89
- 19 Verwey, H & Sars, C M P M, Phase formation in the system Na<sub>2</sub>O Al<sub>2</sub>O<sub>3</sub>–CaO Al<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> at 1200°C in air *J Am Ceram Soc*, **69** (1986) 94–8
- 20 Weisweiler, W & Ahmed, S J, Kinetics of the solid state reactions in the system CaO–Al<sub>2</sub>O<sub>3</sub> *Zem -Kalk-Gips*, **33**(2) (1980) 84–9
- 21 Franken, P E C & Gehrng, A P, Grain boundary analysis of magnesia-doped alumina *J Mater Sci*, **16** (1981) 384–8