Reactions in the CaO-Cs₂O-Al₂O₃ system at 900 degrees C

Citation for published version (APA):

Hoek, van, J. A. M., Loo, van, F. J. J., Wolff, L. R., & Metselaar, R. (1989). Reactions in the CaO-Cs₂O-Al₂O₃ system at 900 degrees C. *Journal of the European Ceramic Society*, 5(2), 93-98. [https://doi.org/10.1016/0955-2219\(89\)90015-0](https://doi.org/10.1016/0955-2219(89)90015-0), <https://doi.org/10.1162/JEEA.2007.5.1.93>

DOI:

[10.1016/0955-2219\(89\)90015-0](https://doi.org/10.1016/0955-2219(89)90015-0)
[10.1162/JEEA.2007.5.1.93](https://doi.org/10.1162/JEEA.2007.5.1.93)

Document status and date:

Published: 01/01/1989

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Reactions in the $\text{CaO}-\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ System at 900°C

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(Received 19 January 1989, revised version received 13 July 1989, accepted 25 July 1989)

Abstract

Reactions in the system $\text{CaO}-\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ 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 $\text{Cs}_2\text{O} \cdot 2\text{CaO} \cdot 4\text{Al}_2\text{O}_3$. 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_2O_3 containing calcia. We found that all calcium aluminates react with Cs_2O forming a stable compound. From these results we conclude that calcium will have a negative effect on the caesium resistance of Al_2O_3 .

Es wurden die Reaktionen im System $\text{CaO}-\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ untersucht. Anhand der experimentellen Ergebnisse wurde ein Kompatibilitätsdiagramm bei 900°C aufgestellt. In diesem System wurde eine neue Phase gefunden, der die Formel $\text{Cs}_2\text{O} \cdot 2\text{CaO} \cdot 4\text{Al}_2\text{O}_3$ zugeordnet wurde. Mittels Röntgenbeugungsdiagrammen wurden die Parameter der Elementarzelle bestimmt.

Aufgrund der Ergebnisse können Aussagen über den Einfluß von Cs auf CaO -haltiges Al_2O_3 gemacht werden. Wir fanden heraus, daß alle Kalziumaluminat mit Cs_2O unter Bildung einer stabilen Verbindung reagieren. Daraus schließen wir, daß Kalzium einen negativen Einfluß auf den Cs-Widerstand von Al_2O_3 hat.

On a étudié les réactions dans le système $\text{CaO}-\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$. 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 $\text{Cs}_2\text{O} \cdot 2\text{CaO} \cdot 4\text{Al}_2\text{O}_3$. 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_2O 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_2O and Al_2O_3 has been done in the past, namely on the $\text{Cs}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ diagram^{1,2}. 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^{3–5}. 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^{6–9}. 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^{10–12}. 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^{13,14} $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3$ (CsA) was made by reacting 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 $\text{CsA} + 4\text{H}_2\text{O} \rightarrow \text{CsA} \cdot 4\text{H}_2\text{O}$ 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 $\text{CaO}-\text{Al}_2\text{O}_3$ 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)^{16,17} The stability of CA_6 at lower temperatures is a point of discussion. This phase is only formed at temperatures above $\pm 1330^\circ\text{C}$,¹⁸ but does not dissociate at lower temperatures.¹⁹ Diffusion couple experiments of CaO against Al_2O_3 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 $\text{C}_{12}\text{A}_7 \gg \text{C}_3\text{A} > \text{CA}_6 > \text{CA}_2 \cong \text{CA}$. Another study showed an increasing amount of CA_6 at expense of CA and CA_2 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

Fig. 1. The $\text{CaO}-\text{Al}_2\text{O}_3$ system according to A. K. Chatterjee and G. I. Zhmoldin¹⁷

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 Cs_2CO_3 (FO Optipur, >99.8%, E. Merck AG, Darmstadt, FRG), CaCO_3 (Zur Analyse, >99%, E. Merck AG, Darmstadt, FRG) and Al_2O_3 (Extrapure, >99.995%, Les Rubis Synthétique des Alpes, Jarrie, France). Because Cs_2CO_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°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 CaCO_3 and Cs_2CO_3 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 Cs_2O 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 Al_2O_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°C , leaving pure Al_2O_3 . So when we heat mixtures of CsA, Al_2O_3 , and the unknown compound for long times, Cs_2O will evaporate out of CsA until no CsA is present. When no Cs_2O

evaporates from the unknown compound, the resulting compositions will lie on a straight line between Al_2O_3 and the unknown compound. Thermogravimetric analyses afterwards showed that indeed no Cs_2O 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_2O content than calculated (34.0 wt% Cs, 10.2 wt% Ca and 28.6 wt% Al). This corresponds best to $\text{Cs}_2\text{O} \cdot 2\text{CaO} \cdot 4\text{Al}_2\text{O}_3$ (CsCa_2Al_4). 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). CsCa_2Al_4 was found to be monoclinic with lattice constants $a = 8.2197 \times 10^{-10} \text{ m}$, $b = 5.2782 \times 10^{-10} \text{ m}$, $c = 7.7639 \times 10^{-10} \text{ m}$, axial angle $\beta = 93.487^\circ$ and the spacegroup probably P2_1 or $\text{P2}_1/\text{m}$.

Table 1. X-ray powder diffraction data of $\text{Cs}_2\text{O} \cdot 2\text{CaO} \cdot 4\text{Al}_2\text{O}_3$

$d_{\text{obs}} (10^{-10} \text{ m})^a$	I/I_1^b	hkl^c	$d_{\text{calc}} (10^{-10} \text{ m})^d$	$d_{\text{obs}} (10^{-10} \text{ m})$	I/I_1	hkl	$d_{\text{calc}} (10^{-10} \text{ m})$
8.204	1.3	100	8.205	1.898.5	2.5	320, 222	1.899.1
7.747	20	001	7.750	1.881.1	5	41 $\bar{1}$	1.881.2
5.476	14	101	5.470	1.861.8	8	32 $\bar{1}$	1.862.8
4.438	35	110	4.439	1.818.6	6	014, 31 $\bar{3}$	1.818.9
4.362	20	011	4.363	1.796.3	2.0	11 $\bar{4}$	1.797.4
4.103	8	200	4.102	1.784.1	8	123	1.784.5
3.908	50	11 $\bar{1}$	3.908	1.768.9	1.0	402	1.768.9
3.875	35	002	3.875	1.754.1	3	41 $\bar{2}$, 114	1.754.5
3.803	2.5	111	3.798	1.733.6	2.5	32 $\bar{2}$	1.734.5
3.723	14	20 $\bar{1}$	3.720	1.723.2	6	313	1.723.4
3.588	5	10 $\bar{2}$	3.589	1.720.5	6	130	1.720.3
3.425.1	45	102	3.424.2	1.711.7	8	22 $\bar{3}$, 204	1.711.8
3.239.1	50	210	3.239.0	1.683.8	6	13 $\bar{1}$	1.684.0
3.121.6	25	012	3.123.5	1.675.4	1.6	131	1.674.9
3.040.4	45	21 $\bar{1}$	3.040.9	1.656.2	2.0	40 $\bar{3}$, 223	1.657.4
2.967.8	70	112	2.967.9	1.619.2	12	420	1.619.5
2.939.1	50	211	2.938.7	1.616.8	12	230	1.617.0
2.906.3	8	20 $\bar{2}$	2.906.5	1.601.2	6	42 $\bar{1}$, 032	1.601.4
2.872.8	14	112	2.872.6	1.590.1	6	23 $\bar{1}$	1.590.5
2.734.9	6	202, 300	2.735.0	1.579.7	8	13 $\bar{2}$, 41 $\bar{3}$	1.580.0
2.639.6	100	020	2.639.1	1.575.3	10	231	1.575.3
2.531.1	3	301	2.531.1	1.567.0	2.0	510	1.566.9
2.511.3	10	120	2.512.3	1.561.7	2.5	024, 32 $\bar{3}$ +	1.561.8
2.498.1	25	021	2.498.2	1.556.5	4	31 $\bar{4}$	1.555.9
2.423.3	8	103	2.422.1	1.548.4	3	12 $\bar{4}$	1.548.2
2.377.3	8	121	2.376.9	1.540.1	1.0	10 $\bar{5}$	1.540.1
2.320.0	12	013	2.320.2	1.520.6	2.0	124, 42 $\bar{2}$	1.520.5
2.281.9	1.3	311	2.282.3	1.484.2	2.5	22 $\bar{4}$	1.483.9
2.265.1	5	11 $\bar{3}$	2.265.3	1.478.9	5	502, 11 $\bar{5}$ +	1.478.8
2.248.9	6	20 $\bar{3}$	2.248.4	1.469.4	1.6	422	1.469.3
2.219.5	12	220	2.219.5	1.454.0	2.5	033, 40 $\bar{4}$	1.453.7
2.200.3	2.0	113	2.201.4	1.448.5	4	115	1.448.5
2.181.1	20	022	2.181.2	1.440.5	3	13 $\bar{3}$	1.440.3
2.151.9	2.5	22 $\bar{1}$	2.152.5	1.424.4	2.5	512, 50 $\bar{3}$ +	1.424.5
2.128.2	1.0	203	2.128.3	1.367.6	2.0	404, 600 +	1.367.5
2.090.2	12	122	2.090.3	1.340.3	2.0	31 $\bar{5}$	1.339.7
2.068.3	2.5	213	2.068.6	1.330.5	2.5	12 $\bar{5}$	1.330.2
2.051.1	8	400	2.051.1	1.324.8	2.0	43 $\bar{1}$	1.324.8
2.009.3	2.5	312	2.009.3	1.320.0	4	040	1.319.6
1.973.7	2.5	213	1.973.9	1.301.4	4	041	1.300.8
1.953.7	8	401, 22 $\bar{2}$	1.953.8	1.291.0	2.0	22 $\bar{5}$, 50 $\bar{4}$ +	1.291.2
1.937.0	10	004, 30 $\bar{3}$	1.937.6	1.278.5	3	134, 43 $\bar{2}$	1.278.3
1.911.7	6	104, 410	1.911.8	1.266.0	2.0	333, 602	1.265.8

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

^a d_{obs} is the observed crystal spacing

^b I/I_1 is the normalized observed intensity

^c hkl are the Miller indices

^d d_{calc} is the calculated crystal spacing

Fig. 2. Representation of some illustrative experiments (●) Starting compositions (CsCO_3 - CaCO_3 - Al_2O_3 mixtures), (○) Cs_2O Al_2O_3 , Al_2O_3 and Cs_2O 2CaO $4\text{Al}_2\text{O}_3$ (samples heated 20h, weights had not stabilized yet), (△) CaO and Cs_2O 2CaO $4\text{Al}_2\text{O}_3$, (□) Al_2O_3 and Cs_2O 2CaO $4\text{Al}_2\text{O}_3$, (×) pure Cs_2O 2CaO $4\text{Al}_2\text{O}_3$. 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_2O starts to evaporate very slowly until no Cs_2O is present at 1500°C . When CsC_2A_4 is left in humid air, it picks up water and loses the crystallinity at the same time.

Fig. 3. Thermogravimetric plot of Cs_2O 2CaO $4\text{Al}_2\text{O}_3$. Heating rate is $5^\circ\text{C}/\text{min}$. 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.

2.2 Compatibility diagram

The experiments discussed so far, produced information about the Cs_2O -rich part of the compatibility diagram. In order to get information about the CaO - Al_2O_3 - CsC_2A_4 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_2CO_3 and heated for 60 h at a temperature of 900°C . C_3A , C_{12}A_7 and CA react with a large excess Cs_2O (50% Cs_2O in overall composition) forming CaO and CsC_2A_4 . When CA_2 , on the other hand, reacts with a large excess Cs_2O , CsC_2A_4 is the only phase detected by XRD. The reactions of the calcium aluminates with smaller amounts Cs_2O 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_2A_4 are used to indicate that, although CsA is not stable at 900°C , CsA and CsC_2A_4 were found together at the beginning of the experiments. Cs_2O will evaporate out of CsA when

Fig. 4. Compatibility diagram at 900°C in the Cs_2O - CaO - Al_2O_3 system. The shaded area is not filled in because it is not completely clarified.

heated for longer times in an open system, leaving Al_2O_3 and evaporated Cs_2O

In the Al_2O_3 -rich part of the diagram, some problems arose. The results of the $\text{CA}_6 + \text{Cs}_2\text{CO}_3$ experiment could not be understood on the basis of the compatibility diagram we constructed. When CA_6 was heated together with Cs_2CO_3 , 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_6 , this compound was heated for 1000 h at 900°C . No signs of decomposition were found. On the other hand CA_6 could not be formed within 1000 h at 900°C out of a $\text{CaCO}_3-\text{Al}_2\text{O}_3$ mixture. Thus, no conclusion about the stability of CA_6 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_2O_3 -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_{11} 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_6 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_2O_3 (Ref. 21) probably leading to the formation of CA_6 . This is the reason why it is important to know the behaviour of this compound when it is exposed to Cs_2O . For this reason we did not want to leave CA_6 out of the diagram, although we do not know the exact phase relations.

As mentioned above, CaO segregates to the grain boundaries of Al_2O_3 . As shown in the experiments, all the calcium aluminates react with Cs_2O to form Cs_2A_4 . 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_2O . 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

The authors gratefully acknowledge E. J. Sonneveld, Technisch Physische Dienst, PO Box 155, Delft, The Netherlands, for determining the cell parameters.

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