JOURNAL OF MATERIALS SCIENCE 17 (1982) 2213–2217

The $K_2O\cdot Al_2O_3$-Al_2O_3 system

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The phase relationships in the system $K_2O\cdot Al_2O_3$–Al_2O_3 between 1200 and 1700° C have been experimentally established. The homogeneity range of potassium β-alumina is limited by the 83 and 91 mol % Al_2O_3 compositions. The eutectic point between the $K_2O\cdot Al_2O_3$ and β-alumina was found to be at 1450° at about 62 mol % Al_2O_3 composition. An X-ray diffraction pattern analysis of potassium β-alumina is shown.

1. Introduction

An increasing interest in the K_2O–Al_2O_3 system has recently been shown [1–3], devoted mainly to attempts to understand the high-temperature corrosion reactions that take place in the channels of the magnetohydrodynamics (MHD) electrical power generator, i.e., interactions between the refractory walls of the MHD device and the potassium in the hot combustion gases that come from the seeding of potassium compounds directly in the plasma and/or from the ash coal. The alkali attack on blast-furnace refractories is one of the most important corrosion factors that affect the production and the life of the blast furnace [4]. Thermodynamic calculations show that potassium and potassium carbonate vapours are mainly the active forms under blast-furnace conditions [5].

Although considerable work has been performed on the Na_2O–Al_2O_3 system, little attention has so far been given to the K_2O–Al_2O_3 system. Much of the interest in the alkali oxide–alumina system stems from the so-called β-alumina phases which, as ionic fast conductors, can be used as solid electrolytes in energy accumulators.

However, despite the fact that it would be of great technological interest, no experimental study of the K_2O–Al_2O_3 system has been published. The only reference the present authors have found in the literature about this system concerns the work of Eliezer and Howald [6]; in their paper a tentative equilibrium diagram is proposed on the basis of a thermodynamic analysis.

The present work focusses on the sub-system $K_2O\cdot Al_2O_3$–Al_2O_3.

2. Experimental procedure

Anhydrous reagent-grade K_2CO_3 and alumina (Fluka, 99.998 % purity) have been used as starting materials. Due to the extreme hygroscopicity of K_2CO_3, and of its reaction products with the alumina, special care in sample preparation and handling was taken.

The starting materials K_2CO_3 and Al_2O_3, stored at 160° C until used, were weighed in a dry balance and the different compositions were mixed in acetone media. The mixtures were then treated at 180° C for 24 h. Pellets of each composition were pressed and preheated at 1000° C in order to precalcine the carbonate. Subsequently, these pellets were encapsulated in platinum crucibles (~ 150 ml) that were sealed to avoid loss of K_2O, held at each temperature during a period ranging from few minutes to 70 h and air-quenched to room temperature in less than ten sec. A molybdenum furnace with temperature control (± 5° C) was used. Samples of different compositions were thermally treated in a temperature interval ranging from 1200° C to 1700° C. The heated samples were mixed with glycerol to avoid rapid hydration and examined by X-ray diffraction analysis.

3. Results and discussion

The results obtained from 11 compositions with molar ratios from 1:1.25 to 1:11 $K_2O\cdot Al_2O_3$ are plotted in Fig. 1. The melting point of $K_2O\cdot Al_2O_3$ of 2260° C, proposed by Roth [7] and in agreement with the data obtained by Cook *et al.* [2] for the $KAlSiO_4$–$KAlO_2$ system, has been adopted.

Taking into account the thermodynamic

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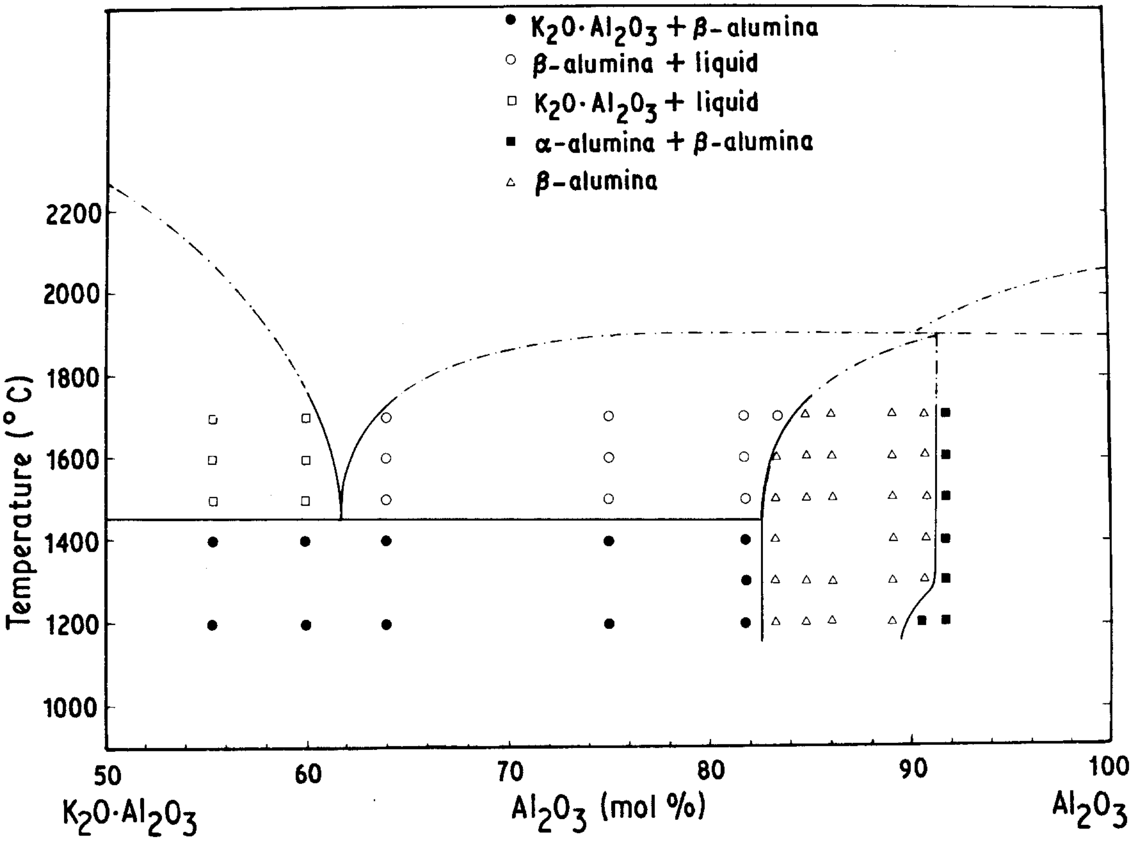

Figure 1 $K_2O \cdot Al_2O_3-Al_2O_3$ phase equilibrium diagram.

analysis made by Eliezer and Howald [6] on the $K_2O-Al_2O_3$ system, it has been assumed that the potassium β-alumina melts incongruently at about 1900° C.

The homogeneity range of β-alumina has been established by holding samples of different compositions for up to 3 days at each temperature, in order to be sure that equilibrium had been reached.

The limits of β-alumina phase solid solution between 1200 and 1600° C ranged from $K_2O \cdot 10Al_2O_3$ to $K_2O \cdot 4.75Al_2O_3$. The potassium β-alumina was found to be isomorphous with the corresponding sodium β-alumina. The presence of the β″ phase has been detected on X-ray powder diffraction patterns by the appearance of the (02.10) line (Miller indices referred to the β″ double-cell), which was identified by comparison with the pattern of Na-β″ alumina.

A least-squares refinement of lattice parameters has been made on data from the $K_2O \cdot 9.5Al_2O_3$ composition using 10 overlap-free reflections indexed on the basis of the sodium β-alumina X-ray diffraction pattern proposed by Théry and Briancon [9]. The results obtained were $a = 0.5609 \pm 0.0005$ nm and $b = 2.268 \pm 0.004$ nm. In Fig. 2 the corresponding pattern is shown. In Table I the interplanar spacings, d, Miller indices, hkl, and the corresponding observed intensities, I_{obs}, are listed.

As in the $Na_2O-Al_2O_3$ system [8], the β″ form is also metastable in the present system and was always found together with the β form below 1550° C.

Roth [7] reported that the eutectic between $K_2O \cdot Al_2O_3$ and β-alumina occurs at 1910° C, but the composition was not established. In that investigation the author did not mention the experimental procedure followed.

In the present work serious difficulties have been found when trying to determine the stability of the different phases in the sub-system $K_2O \cdot Al_2O_3-\beta Al_2O_3$, such as the impossibility of trying to prepare highly polished samples for analysis by reflected-light microscopy, due to the high hygroscopicity of these kinds of samples. However, the main problem was that in the first round of 2 h firing, which had been sufficient

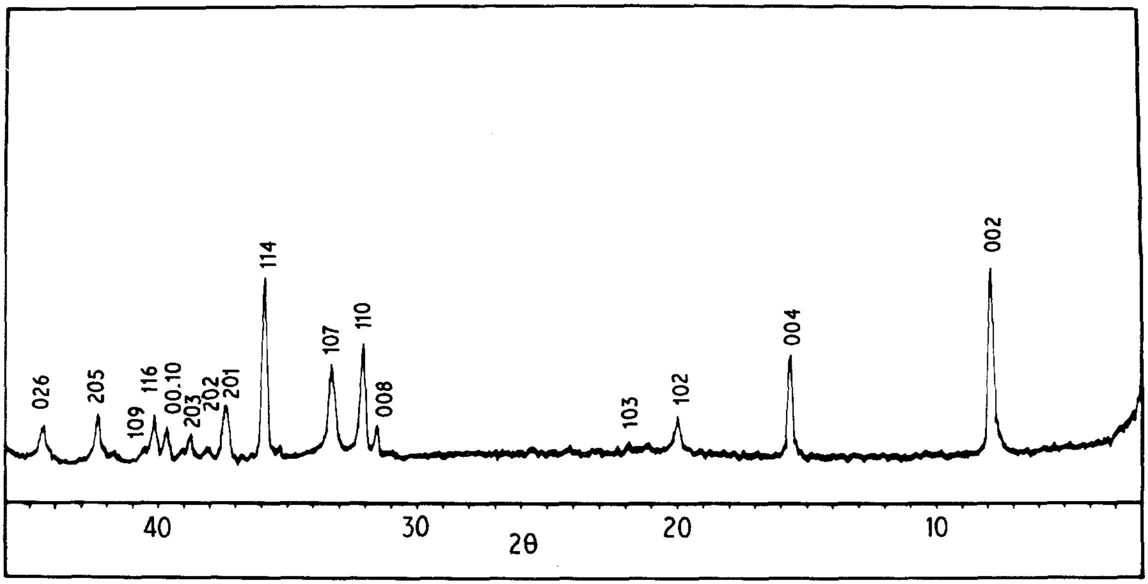

Figure 2 X-ray diffraction pattern corresponding to β-K_2O·9.5Al_2O_3.

to reach equilibrium in the homogeneity range of β-alumina, K_2O·Al_2O_3 and β-alumina were found by X-ray diffractions at all compositions and temperatures tested.

At temperatures up to 1450° C, K_2O·Al_2O_3 and β-alumina were detected by X-ray diffraction, in all compositions in a ratio corresponding to its situation in the diagram. At higher temperatures the results were more confusing.

TABLE I X-ray diffraction data for β-K_2O·9.5 Al_2O_3

d^*	hkl	I_{obs}
11.34	0 0 2	100
5.67	0 0 4	50
4.46	1 0 2	20
4.08	1 0 3	4
2.83	0 0 8	17
2.80	1 1 0	60
2.69	1 0 7	50
2.51	1 1 4	100
2.41	2 0 1	30
2.37	2 0 2	7
2.31	2 0 3	14
2.26	0 0.1 0	18
2.25	1 1 6	25
2.23	1 0 9	5
2.14	2 0 5	18
2.04	2 0 6	20
1.94	2 0 7	8
1.84	2 0 8	2
1.62	0 0.1 4	6
1.61	3 0 1	7
1.59	2 1 7	20
1.56	1 1.1 2	15
1.55	3 0 4	10
1.48	3 0 6	4
1.41	0 0.1 6	14
1.39	2 2 1	80

*The calculated d-values were found to be very close the observed d-values.

This behaviour could be due to the following:

(a) both K_2O·Al_2O_3 and β-Al_2O_3 are stable in the tested temperature range:

(b) devitrification took place during quenching; and

(c) equilibrium was not reached due to the kinetics of the process.

In order to determine the equilibrium in the temperature interval 1400 to 1700° C, a study of the phase composition after isothermal treatment against time was followed by X-ray diffraction analysis. The intensities of the (002) peak for β-alumina and (220) peak for K_2O·Al_2O_3 were taken as references. The results obtained for 60, 64 and 75 mol% Al_2O_3 compositions are shown in Fig. 3. In the composition corresponding to 60 mol% Al_2O_3, at 1400° C, the K_2O·Al_2O_3 and β-alumina are stable and the relation between both is in agreement with the position of this composition in the diagram. However, at 1600° C, K_2O·Al_2O_3 is the only phase that remains stable, while the amount of β-alumina is negligible, probably due to a devitrification phenomenon.

In the 64 mol% Al_2O_3 composition, a situation similar to the previous one is observed at 1400° C. Conversely, at 1500, 1600 and 1700° C the K_2O·Al_2O_3 phase is the metastable one and tends to disappear at a rate which is directly proportional

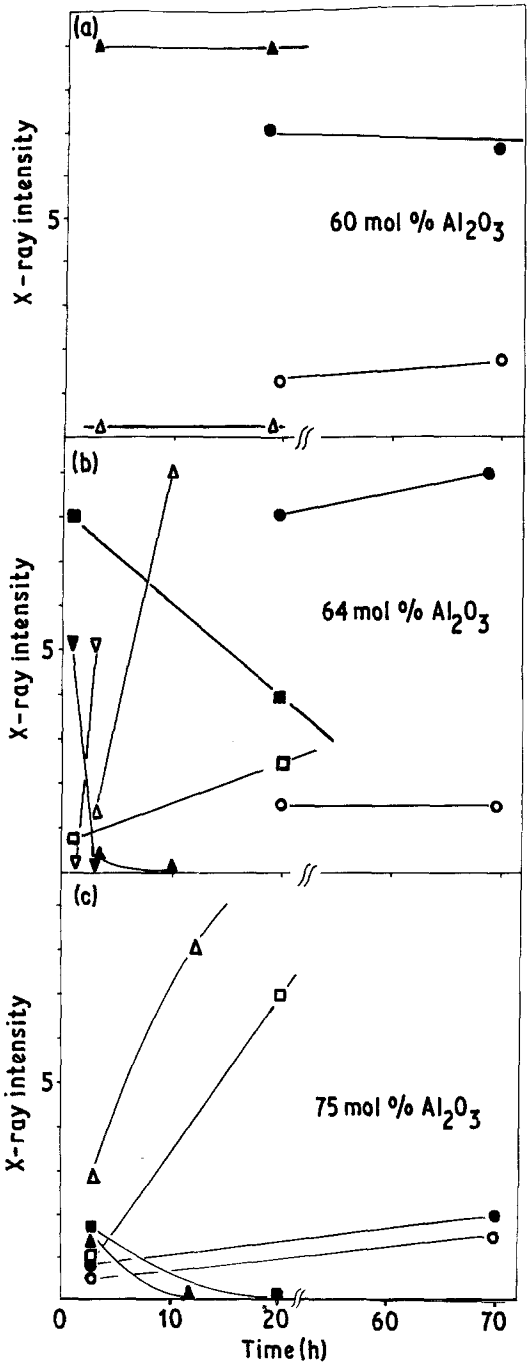

Figure 3 Phase evolution plotted against time at different temperatures for (a) 60 mol% Al_2O_3, (b) 64 mol% Al_2O_3 and (c) 75 mol% Al_2O_3. ●: $K_2O{\cdot}Al_2O_3$, 1400° C; ○: β-alumina, 1400° C; ■: $K_2O{\cdot}Al_2O_3$, 1500° C; □: β-alumina, 1500° C; ▲: $K_2O{\cdot}Al_2O_3$, 1600° C; △: β-alumina, 1600° C; ▼: $K_2O{\cdot}Al_2O_3$, 1700° C; ▽: β-alumina, 1700° C.

to the magnitude of the treatment temperature. Consequently, β-alumina is the stable phase. A similar behaviour is observed for the 75 mol% Al_2O_3 composition.

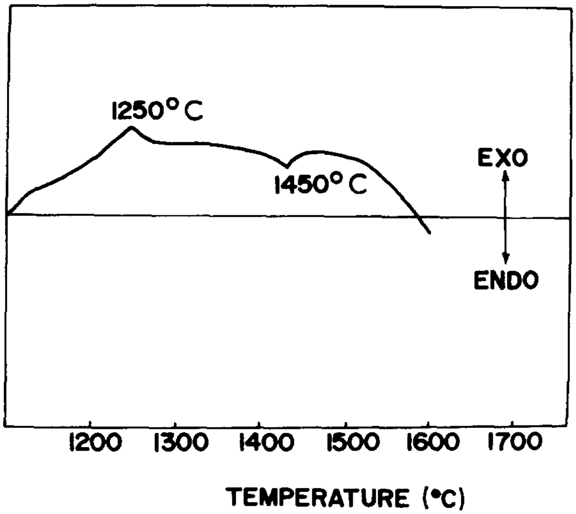

Figure 4 Differential thermal analysis corresponding to 60 mol% Al_2O_3 composition.

These results suggest that the eutectic temperature must be located between 1400 and 1500° C, with a composition of about 62 mol% Al_2O_3.

The differential thermal analysis trace, performed on the 60 mol% Al_2O_3 composition is shown in Fig. 4. The exothermic peak that appears at 1200° C may correspond to the formation of aluminates while the endothermic peak at 1450° C is probably due to the appearance of liquid at the eutectic temperature. This latter temperature is in agreement with the temperature range previously mentioned.

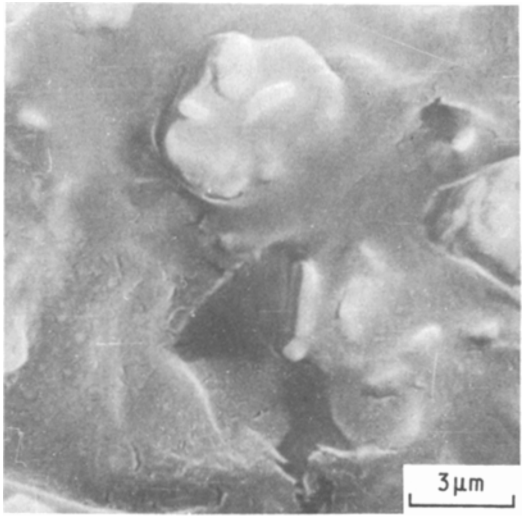

Figure 5 Scanning electron micrograph corresponding to the fracture surface of 64 mol% Al_2O_3 composition treated at 1650° C.

The fracture surface of samples treated at 1650° C in the primary field of β-alumina has been studied by scanning electron microscopy. In Fig. 5 small crystals (of size $< 3\,\mu$m) of β-alumina in an amorphous matrix can be observed.

In summary, it can be concluded that the homogeneity range of β-alumina is limited to between 83 and 91 mol% Al_2O_3 and that the temperature and composition of the eutectic between β-alumina and $K_2O \cdot Al_2O_3$ are 1450° C and about 62 mol% Al_2O_3, respectively.

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Received 5 June
and accepted 15 December 1981