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 \( \beta \)-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 \( \beta \)-alumina was found to be at 1450 °C at about 62 mol % \( Al_2O_3 \) composition. An X-ray diffraction pattern analysis of potassium \( \beta \)-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 \( \beta \)-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 focuses 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 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
analysis made by Eliezer and Howald [6] on the K₂O-Al₂O₃ 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 K₂O·10Al₂O₃ to K₂O·4.75Al₂O₃. 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 K₂O·9.5Al₂O₃ 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, \( I_{\text{obs}} \), are listed.

As in the Na₂O-Al₂O₃ 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 K₂O·Al₂O₃ 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 K₂O·Al₂O₃–βAl₂O₃, 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...