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Effect of electric fields on solid-state reactions between oxides

Part 2 *Interdiffusion studies in polycrystalline calcium and aluminium oxide pellets*

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A study of the effect of d.c. electric fields on the interdiffusion behaviour of CaO and Al_2O_3 pellets was made using scanning electron microscopy, electron microprobe analysis and X-ray diffraction. When the CaO component is positively charged, the field acts to reinforce the preferred direction of normal thermal diffusion and the thickness of the product layers is increased. The reverse occurs when the CaO component is negatively charged. A greater degree of diffusion is observed in unelectrolysed than in electrolysed samples; this unexpected result could be due to field-enhanced sintering in the latter which reduces the contribution of grain-boundary diffusion processes. The effective electrical mobility of the migrating species in the various product phases is calculated from the measured downfield shift in the diffusion profile, and compares well with estimates previously made by more approximate methods.

1. Introduction

In Part 1 of this paper [1] it was shown that the formation of calcium aluminates from the oxides can be enhanced by subjecting the system to d.c. electric fields. The enhancement is particularly marked at the positive electrode. One of the most important ways in which electric fields can influence diffusion-controlled reactions is by displacing the diffusion profile downfield by an amount Δ which is related [2] to the effective electrical mobility of the migrating species (μ_{eff}), the field strength E and the diffusion time t:

$$\Delta = \mu_{\mathrm{eff}} E t. \qquad (1)$$

Of the few measurements of Δ which have been reported, most have been made on simple single-crystal systems (e.g. KCl–KBr single crystals [3]), and no work appears to have been done on oxides, either single crystal or polycrystalline.

The aim of this study was to investigate the effect of electric fields on the interdiffusion profile of the calcium oxide–aluminium oxide system. Polycrystalline compacts were studied in preference to single crystals, to make the results more directly relevant to previous work on practical systems [1, 4, 5], even though results obtained from polycrystalline samples are subject to grain-boundary effects and are less amenable to precise theoretical treatments.

Since the CaO–Al_2O_3 system is complex, forming many aluminate phases, both electron microprobe analysis and X-ray diffraction was used, in order to investigate the phase composition of the reaction zone as well as the chemical composition within the pellets.

2. Experimental

The materials used in this work have been described previously [1]. Pellets of CaO and Al_2O_3 of 20 mm diameter by 5 mm high were pressed without binder at 5×10^3 kg cm^{-2} and separately prefired at 1100° C for 3 h to remove any volatiles and induce some densification. The pellets were then placed in close contact between two platinum

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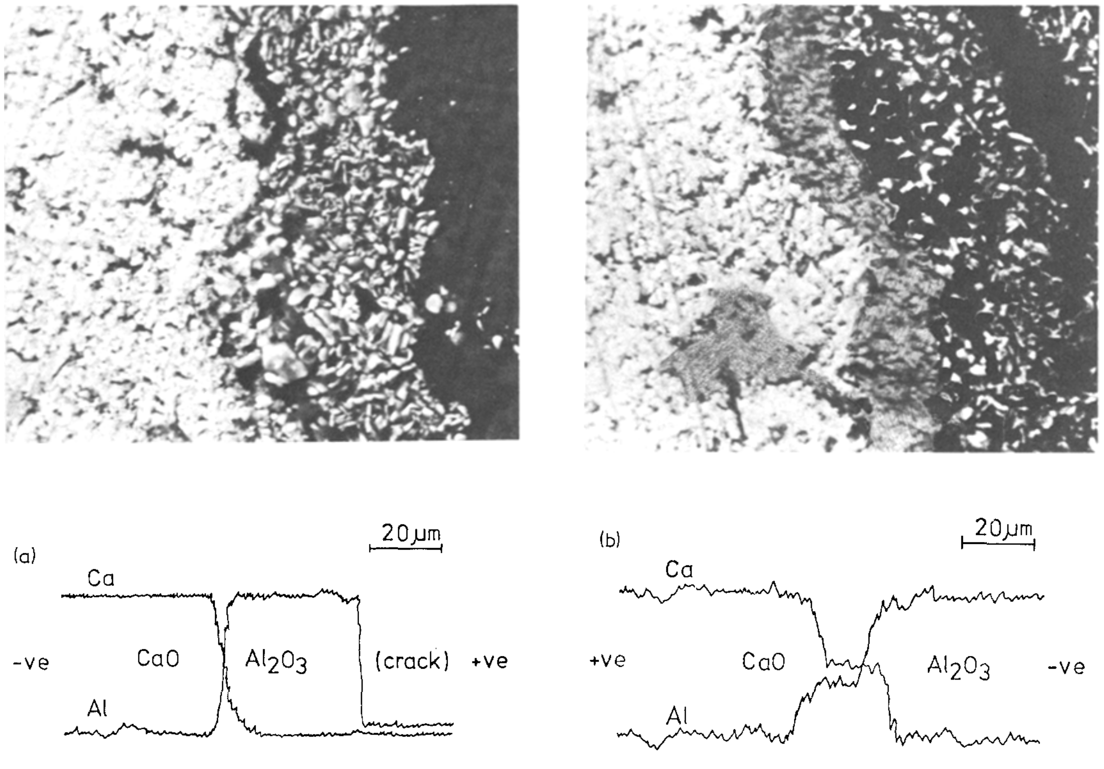

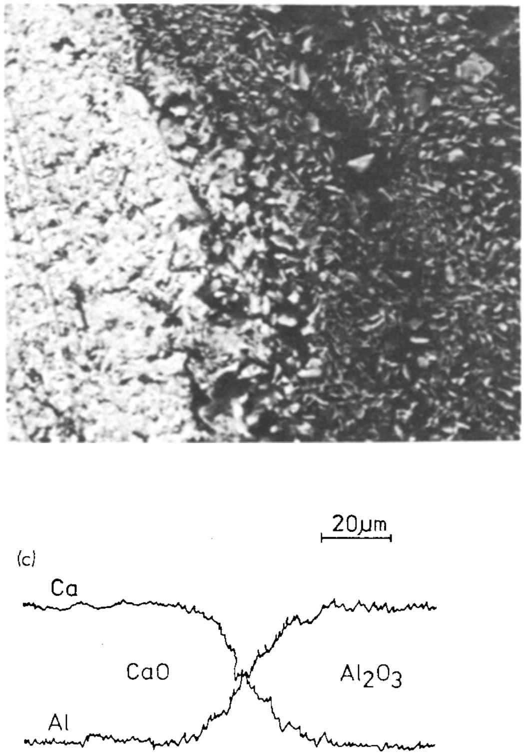

Figure 1 Compositional electron micrographs and elemental line scans across the reaction zone of electrolysed and unelectrolysed CaO–Al_2O_3 diffusion couples. Reaction time = 4.0 h, temperature = 1250° C, field strength = 6.0×10^4 V m^{-1}. (a) CaO – ve, (b) CaO + ve, (c) Unelectrolysed.

foil electrodes supported by alumina ceramic pressure plates, wired tightly together with platinum wire and annealed at 1250 to 1300° C for 4 to 56 h. In several of the runs, platinum wire markers were inserted between the pellets before firing. An electric field of 6.0×10^4 V m^{-1} from a Philips PE 4839 E.H.T. power supply was established across the electrodes, experiments being made in which the polarity of the CaO pellets was both negative and positive with respect to the Al_2O_3 pellet. Unelectrolysed control experiments were also made. After firing, the samples for microprobe analysis were sectioned across their diameter, embedded in epoxy resin, then ground and polished and coated with a thin-vacuum-deposited carbon film. The microprobe analyses were made with a JEOL JXA 50-A combined scanning electron microscope and microprobe analyser.

The pellet samples for X-ray diffraction were separated at the interface and mounted on glass slides with epoxy resin. The reaction faces were then examined using a CGR model GS-2000 high precision horizontal goniometer, thin layers being progressively ground off and the thickness measured by micrometer. Semi-quantitative estimates of the various reactant and product phases were thus made as a function of the distance from the interface, on the basis of relative peak intensities. In the absence of an internal standard, considerable care was taken to ensure that the pellet was re-mounted precisely in the goniometer after each grinding. The same diagnostic peaks as previously described [1] were adopted for each phase.

3. Results and discussion

3.1. Electron microprobe analyses

Compositional micrographs of the reaction zones of typical samples annealed at 1250° C for 4 h are shown in Fig. 1, which also includes elemental line scans for Ca and Al taken across the reaction zone.

All the samples cracked and shrank apart on cooling, the crack occurring in each case in the alumina pellet rather than at the reaction zone, which remained intact. Fig. 1 shows that when the CaO side of the couple is negatively charged, diffusion of Ca into Al_2O_3 is suppressed, as would be expected, since in this case the field tends to oppose the normal direction of thermal diffusion (Ca into Al_2O_3 [6]). When the polarity is reversed, significant diffusion of Ca into Al_2O_3 is observed. However, the unexpected result is that in the unelectrolysed control a greater degree of diffusion is observed than in the electrolysed samples, even when the field direction in the latter is such as to reinforce normal thermal diffusion. One possible explanation for this result might be the significantly greater degree of intergranular sintering which was observed in the electrolysed samples, particularly in the CaO component. Such sintering would tend to hinder grain-boundary diffusion, which has been suggested [6] to play an important role in the interdiffusion mechanism between CaO and Al_2O_3 polycrystalline pellets. In the samples reacted for 4 h, the diffusion layer was too poorly developed to allow the identification of discrete regions of different phases, as was reported in the study by Kohatsu and Brindley [6] of unelectrolysed CaO–Al_2O_3 pellets. Diffusion couples for X-ray identification of the phase compositions were, therefore, fired for much longer times (56 h) and higher temperature (1300° C) to ensure good development of all the aluminate phases within the reaction zone.

3.2. X-ray diffraction analyses

The results of a typical experiment are given in Figs. 2 to 4. Fig. 2 shows the concentration profiles of CaO and Al_2O_3 as a function of distance from the reaction face. Under these conditions of reaction time and temperature, the diffusion direction is more predominantly Ca into Al_2O_3 than vice versa, confirming the present electron microprobe results, and those of Kohatsu and Brindley [6]. It should be noted, however, that some doubt existed as to the precise location of the pellet interface in some of the present experiments, although the pellets separated in the vicinity of the platinum marker in most cases. The measurements shown in Figs. 2 to 4 were made with respect to the point at which the pellets

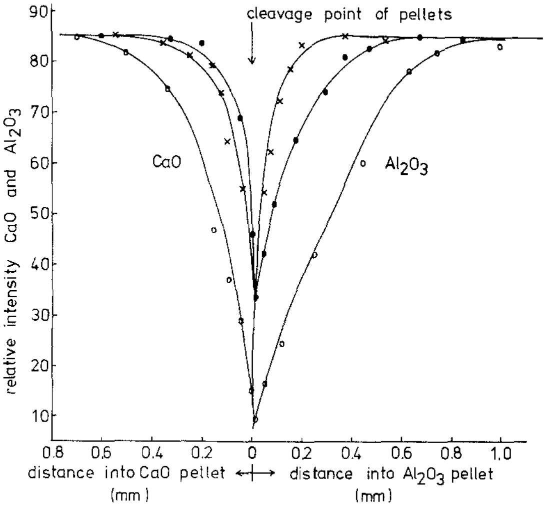

Figure 2 Concentration profile of CaO and Al_2O_3 in the reaction zone of electrolysed and unelectrolysed CaO–Al_2O_3 diffusion couples. Reaction time = 56 h, temperature = 1300° C, field strength = 6.0×10^4 V m^{-1}. x = CaO side of couple +ve, ● = CaO side of couple –ve, o = unelectrolysed.

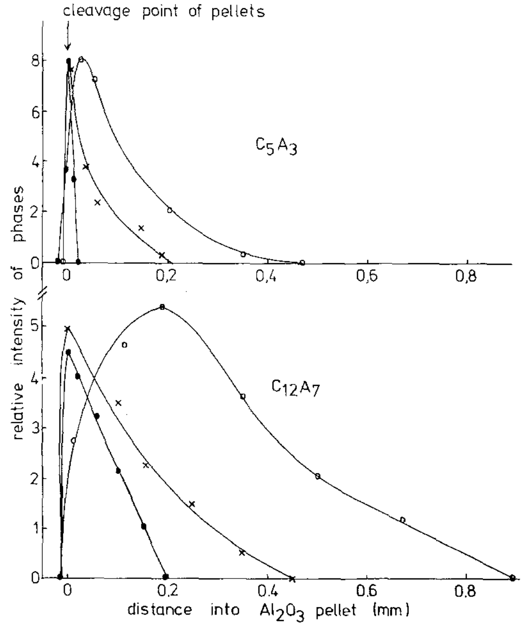

Figure 3 Concentration profiles of C_5A_3 and $C_{12}A_7$ in the reaction zone of electrolysed and unelectrolysed $CaO-Al_2O_3$ diffusion couples. Reaction time = 56 h, temperature = 1300° C, field strength = 6.0×10^4 V m^{-1}. x = CaO side of couple +ve, ● = CaO side of couple −ve, o = unelectrolysed.

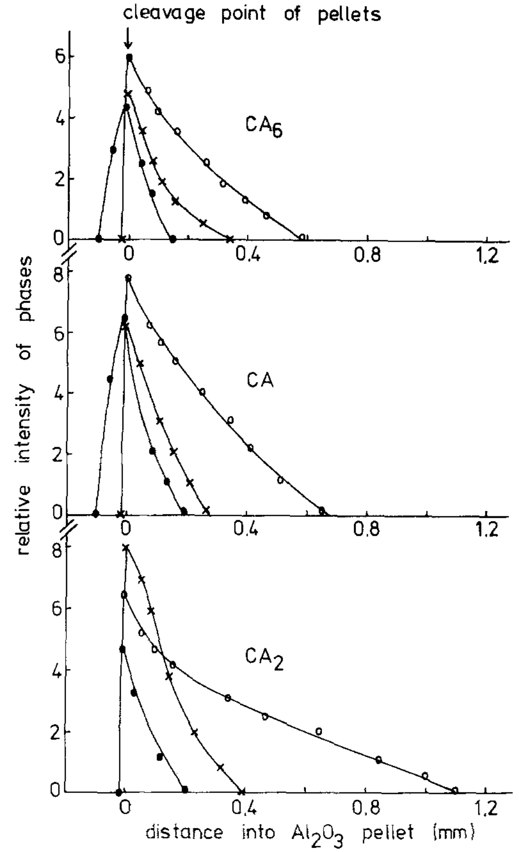

Figure 4 Concentration profiles of CA_6, CA and CA_2 in the reaction zone of electrolysed and unelectrolysed $CaO-Al_2O_3$ diffusion couples. Reaction time = 56 h, temperature = 1300° C, field strength = 6.0×10^4 V m^{-1}, x = CaO side of couple +ve, ● = CaO side of couple −ve, o = unelectrolysed.

separated, which as far as could be ascertained from the position of the markers was reasonably close to the original pellet interface.

As in the electron microprobe studies, the greatest degree of diffusion of Ca into Al_2O_3 occurred in the absence of electric fields, resulting in a greater depth of formation of all the aluminate phases in the unelectrolysed samples (Figs. 3 and 4). This is also reflected in Fig. 2 in the greater depletion of CaO and Al_2O_3 in the areas adjacent to the reaction zone. The omission of C_3A from Figs. 3 and 4 is due to the fact that this phase was not observed in significant amounts in any of the samples, and in those cases where it was observed, its concentration tended to fluctuate in a random manner, unlike the regular changes in concentrations of the other aluminate phases.

In the electrolysed samples, the thickness of the aluminate phase layer was greatest when the Al_2O_3 pellet was negatively charged, consistent with the suggestion [5] that under these conditions the preferred direction of thermal diffusion is reinforced by the field, which assists the movement of the most mobile species (in this case Ca) into Al_2O_3. When the CaO pellet is negatively charged, the field opposes the movement of Ca in this direction and the thickness of the aluminate product layer is significantly smaller, and not particularly influenced by the polarity of the field.

These observations on the thickness of the aluminate phases are consistent with the depletion of Al_2O_3 in that side of the reaction couple (Fig. 2). Similar reasoning for the Ca side of the couple would predict that the depletion zone of CaO should be greatest when the CaO pellet is negatively charged. In practice, the difference between the depletion zone thickness when the CaO is positively or negatively charged is very small (Fig. 2), again consistent with only a small degree of counter-diffusion of Al into CaO.

Figs. 3 and 4 show that in the absence of the electric field, the relative penetration depth of the various aluminate phases into the Al_2O_3 pellet is greatest for CA_2 and decreases in the order $C_{12}A_7 > CA > CA_6 > C_5A_3$. This order is different from the order observed by Kohatsu and Brindley [6] ($C_{12}A_7 > C_3A > CA_6 > CA_2 = CA$) which was also in reasonably good agreement with the order of increasing oxygen ion packing density in these aluminate phases. On the other hand, the situation is different in the electrolysed samples, which follow an approximate order of decreasing phase thickness $C_{12}A_7 > CA_2 \simeq CA > CA_6 > C_5A_3$ irrespective of the polarity. This order is closer to that predicted from oxygen packing densities, suggesting that in the unelectrolysed samples, some additional factor other than oxygen packing density is also operating. Such a factor could well be the previously suggested modification of grain-boundary diffusion in the compacts by sintering, which is expected to be more pronounced in the electrolysed samples due to enhanced mass transfer across the reaction zone and the possibility of electrical heating. Thus, the results obtained for the electrolysed samples are more likely to be controlled by the bulk properties of the various phases, whereas the behaviour of the unelectrolysed samples is more likely to be controlled by the properties of the grain boundaries.

3.3. Effective electrical mobility of the migrating species

The present results for the electrolysed samples provide a measure of Δ, the downfield shift of the diffusion profile due to the electric field, from which the effective electrical mobility of the migrating species, μ_{eff}, can be derived (Equation 1). Since the foregoing discussion suggests that the electrolysed samples may behave more like single crystals than do the unelectrolysed samples in which grain-boundary diffusion may predominate, and further, that counter-migration of Al into CaO is apparently insignificant under conditions of reversed polarity, it appears reasonable that Δ might best be estimated from the difference in the thickness of the aluminate product layers under the two different polarity conditions. Values of the downfield shift Δ thus calculated for the various aluminate phases are shown in Table I, which also includes values of μ_{eff} derived from Equation 1.

TABLE I Diffusional shift distances (Δ) and effective electrical mobilities (μ_{eff}) for the various aluminate phases. Field strength = 1.6×10^3 V cm^{-1}, reaction time = 2.02×10^5 sec.

Phase	Δ (cm)	μ_{eff} (cm sec^{-1} (V cm^{-1})$^{-1}$)
$C_{12}A_7$	2.5×10^{-2}	7.7×10^{-11}
CA_2	2.0×10^{-2}	6.2×10^{-11}
CA	8.0×10^{-2}	2.5×10^{-11}
CA_6	1.9×10^{-2}	5.9×10^{-11}
C_5A_3	1.75×10^{-2}	5.4×10^{-11}

Table I shows that the effective mobilities thus calculated for the migrating species are similar in all the aluminate phase, and have a value of about 6×10^{-11} cm sec^{-1} (V cm^{-1})$^{-1}$. This is within an order of magnitude of the value calculated for C_3A (1.5×10^{-11} cm sec^{-1} (V cm^{-1})$^{-1}$) [5] by assuming that μ_{eff} is related to the true electrical mobility μ and the electrical conductivities of the aluminate phase (σ) and the pure oxide (σ_0) by:

$$\mu_{eff} = (\sigma_0/\sigma)\mu. \qquad (2)$$

Although the phase C_3A was not positively identified in all of the present diffusion couples, the similarity in the values of μ_{eff} for all the other aluminate phases suggests that μ_{eff} for this and other cement clinker phases [5] therefore appear to be justified and the mechanistic conclusions drawn from these calculations are probably also soundly based.

4. Conclusions

(1) Interdiffusion between pellets of CaO and Al_2O_3 can be influenced by externally applied d.c. electric fields. When the CaO component is positively charged, the thicknesses of the zones of product phases are greater than when the CaO pellet is negatively charged. Since the preferred direction of normal thermal diffusion in this system is Ca into Al_2O_3, the field acts to either reinforce or oppose this process when the Al_2O_3 is respectively negatively or positively charged.

(2) The degree of interdiffusion in unelectrolysed samples is in all cases greater than for the electrolysed samples. S.E.M. evidence suggests

that this unexpected result may be due to enhanced sintering in the electrolysed samples, in which grain-boundary diffusion would thereby be reduced.

(3) Calculations of the effective electrical mobility of the migrating species made from measurements of the field-induced shift in the diffusion profile are within an order of magnitude of previous estimates of the same parameter made from electrical conductance measurements.

References

1. K. J. D. MacKENZIE, R. K. BANERJEE and M. R. KASAAI, *J. Mater. Sci.* **14** (1979) 333.
2. F. A. KROGER, "The Chemistry of Imperfect Crystals", 2nd Edn, Vol. 3 (North Holland, Amsterdam, 1974) pp. 25–33.
3. Ya. E. GEGUZIN, V. I. SOLUNSKII and Yu. I. BOIKO, *Sov. Phys. Solid State* 8 (1966) 1046.
4. K. J. D. MacKENZIE and R. A. FLETCHER, *Thermochim. Acta* (in press).
5. K. J. D. MacKENZIE, *ibid.* (in press).
6. I. KOHATSU and G. W. BRINDLEY, *Z. Phys. Chem. Neue Folge* **60** (1968) 79.

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