Oxide-Oxide Interactions Studied by Transmission Electron Microscopy

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The use of electron diffraction to study the interface region of thin, composite oxide films provides a sensitive means of investigating the mechanism of the solid-state reactions between these oxide layers.

An investigation of the reaction between CuO and Al_2O_3 and NiO and Al_2O_3 by this method indicates the formation of an aluminate layer by a mechanism involving cation counterdiffusion.

1. Introduction

Present-day techniques for the formation of metal-ceramic seals are confined mainly to the "active metal" and "sintered powder" (or "refractory metal") processes. The latter process, a direct outgrowth of one of the earliest sealing techniques, consists of sintering a refractory metal coating onto a ceramic surface, followed by the brazing of the metallised ceramic to the metal valve component. Although a number of refractory metals have been used in seal formation by this process, Mo and a Mo-Mn mixture (4:1) have proved most successful and are most widely used by the electronics industry today.

Briefly, the process consists of coating the cleaned ceramic surface with a finely dispersed powder of Mo (or Mo-Mn) held in a suitable suspension of nitrocellulose lacquer. This coated surface is fired in a hydrogen atmosphere at a temperature between 1300 and 1500° C and a layer of Cu or Ni is then applied to this sintered powder layer, usually by electroplating. Finally, this metallised ceramic is brazed to the metal part of the valve component.

A number of workers have indicated the presence of a metal oxide in the metallising layer during this sealing process. Pincus [1] first described the role that MnO, formed during heating in a moist hydrogen atmosphere, played in the formation by the Mo-Mn process of

successful Al_2O_3-metal seals. In a later series of experiments [2], he demonstrated the increased adherence of Al_2O_3-Mo seals formed upon the addition of MoO_3 to the Mo. Denton and Rawson [3] later substantiated these findings. These experiments appeared to indicate that, during seal formation by the refractory metal process, the refractory powder was bonded to the ceramic surface via an intermediate, metal oxide layer. The success of the bond was dependent, therefore, on (i) the bonding of the metal to this intermediate oxide layer, and (ii) the adhesion of this oxide layer to the ceramic surface.

On the basis of these experimental findings, the present research was initiated to investigate this oxide-oxide interface. Various metal oxide-Al_2O_3 interfaces were synthesised in the form of thin films suitable for examination by transmission electron microscopy and selected-area electron diffraction.

2. Experimental Method

The systems studied were CuO and NiO on α-Al_2O_3. Suitable films of α-Al_2O_3 for investigation by transmission electron microscopy were prepared in the following manner. A strip of 99.99% purity Al was electropolished in a perchloric acid-ethanol solution and then anodised in an electrolyte of 48 g of Na_2HPO_4, 400 ml of water, and 2 ml of concentrated

sulphuric acid. A layer of Al_2O_3 was formed on the Al surface, the thickness of which was proportional to the applied voltage (1 V $\simeq$ 14 Å of Al_2O_3). Films formed at 40 V were found suitable for the present work. After washing in dilute hydrochloric acid, the oxide film in the form of squares $\frac{1}{2}$ cm $\times$ $\frac{1}{2}$ cm was stripped from the surface of the Al by scratching through the oxide layer, and immersing the specimen first in a saturated solution of mercuric chloride, and then in a dish of distilled water. The mercuric chloride tended to undermine the oxide layer by amalgamating with the Al underneath. On immersion in water, individual oxide squares floated to the surface, where they were removed by collection on Pt grids.

The oxide film so formed was amorphous in structure and had to be crystallised by heating at 1250° C for 1 h, when α-Al_2O_3 was formed.

Cu and Ni were then evaporated onto this α-Al_2O_3 film to give a calculated film thickness of $\simeq 100$ Å. The composite film was heated at the chosen reaction temperature in an oxidising atmosphere, when the metal rapidly transformed to the oxide. In some cases, agglomeration occurred during heating, giving rise to individual oxide particles about 1000 Å in diameter. After allowing time for reaction between the oxides, the specimen was examined by transmission in the electron microscope. Because of the insulating properties of the oxides, charging occurred during examination, which gave rise to an unsteady image. To overcome this difficulty, a thin layer of carbon was evaporated onto the specimen prior to examination.

3. Results

Copper-coated films of Al_2O_3 were heated in air for various times at temperatures between 680 and 850° C. Heating of the films at 680° C gave rapid oxidation of the Cu particles to CuO, but further reaction at the CuO-Al_2O_3 interface was limited. Even after prolonged heating (50 h at 680° C), there was no electron diffraction evidence of any new phase on the larger α-Al_2O_3 crystals. The CuO particle size appeared constant for films heated at this temperature for various times (fig. 1).

Micrographs of films heated at 750 and 850° C for various times are shown in figs. 2 and 3. Considerable $CuAl_2O_4$ was detected by electron diffraction in the 750° C, 6 h sample; and again contrast effects associated with this new phase were observed. Comparison of unreacted and re-
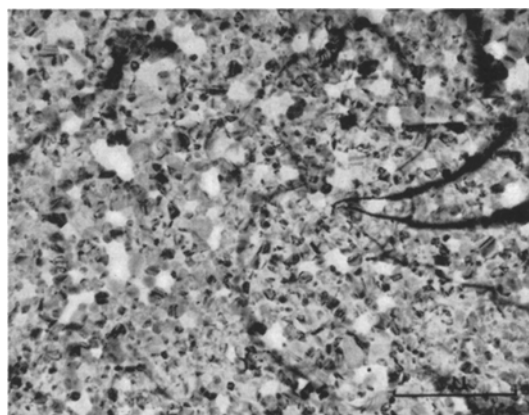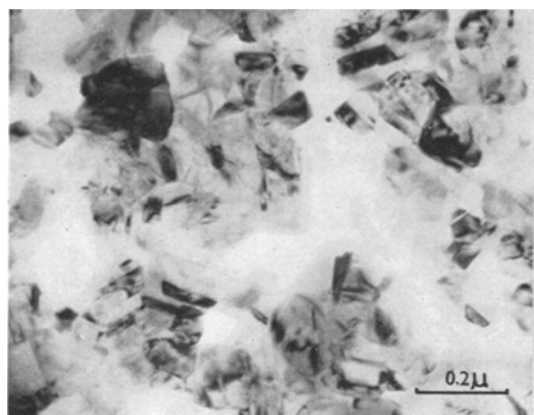

Figure 1 Transmission electron micrograph of CuO: α-Al_2O_3 composite film formed by evaporation of Cu onto thin section α-Al_2O_3 substrate followed by heating in air at 680° C for 5 min. Al_2O_3:CuO interface regions appear quite featureless. Twins within the CuO particles have formed during their growth.

acted CuO regions of the 23 h specimen further indicated these effects (fig. 2). There also appeared to be a difference in size between the newly formed $CuAl_2O_4$ regions and the unreacted CuO regions, suggesting that surface diffusion was involved during reaction. Electron diffraction examination indicated a random orientation of the aluminate regions relative to the alumina substrate. The reacted regions of the films heated at 850° C (fig. 3) were similar in appearance to those found after treatment at 750° C.

Occasionally, CuO particles were observed to nucleate and grow on the Al_2O_3 film edge, thus allowing a direct examination of the interface region parallel to the boundary. An example of this is shown in fig. 4 from a specimen heated at 850° C for $2\frac{1}{4}$ h. Analysis of the selected-area diffraction pattern from the particle sitting on the Al_2O_3 film edge and the corresponding dark-field micrograph taken with one of the aluminate reflections, given in fig. 4b, indicated it to be $CuAl_2O_4$ (fig. 4c). In view of the morphology, the formation of this new phase must have involved the diffusion of Al^{3+} ions out from the Al_2O_3 lattice.

Observations on NiO-Al_2O_3 films were confined to specimens heated at 920° C for 75 h. Again, reaction of the NiO and Al_2O_3 phases resulted in the formation of $NiAl_2O_4$, the appearance of this phase being similar to the $CuAl_2O_4$ regions (fig. 5). It would appear reasonable to assume that the mode of alum-

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(a)
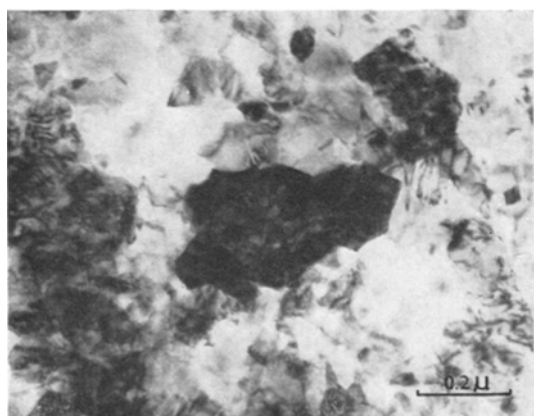
(b)

Figure 2 Transmission electron micrographs of α-Al₂O₃: CuO films heated in air at 750° C for 23 h: (a) a region of CuO and α-Al₂O₃ only; (b) a region of CuAl₂O₄ and α-Al₂O₃. There appears to be a difference in size between the reacted and unreacted particles.

inate formation was the same for both systems.

4. Discussion

Observations on the CuO-Al₂O₃ films heated at 850° C for 2¼ h (fig. 4) indicated that migration of Al³⁺ and Cu²⁺ ions was involved in the oxide-oxide reaction to form the spinel phase. A cation counterdiffusion mechanism for solid-state reactions involving halide systems was first suggested by Koch and Wagner [4]. Later work by other investigators on a number of oxide-oxide systems indicated an alternative reaction mechanism, namely the diffusion of anions and cations of one species into the more stable lattice of the other. The work of Benston and Jagitsch [5], Linder *et al* [6-9], and Branson [10] indicated that this latter mechanism was
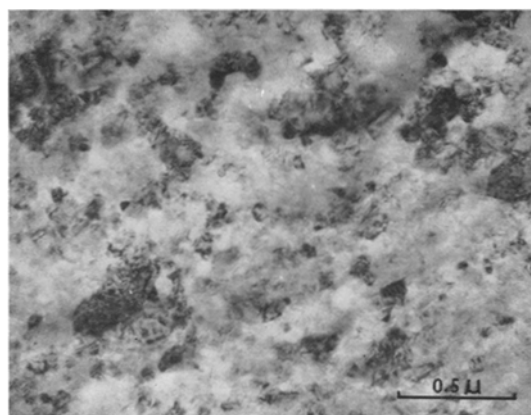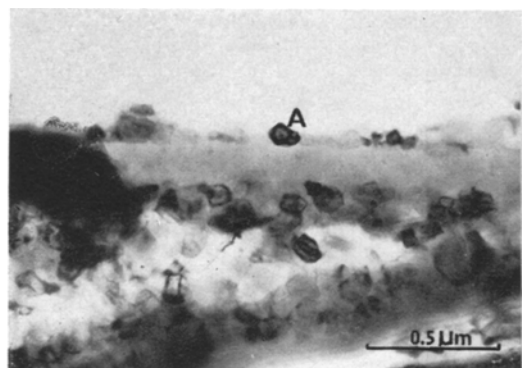

Figure 3 Transmission electron micrograph of an α-Al₂O₃: CuO film heated in air at 850° C for 1 h. Selected-area diffraction indicated the presence of CuAl₂O₄ and α-Al₂O₃ only. No unreacted CuO regions were identified. An imperfect, crystalline, spinel-product layer is suggested by the observed contrast effects.

operative for the systems ZnAl₂O₄ and NiAl₂O₄. These findings were based on marker and kinetic studies of the reactants. However, Linder and coworkers found that, for other systems (ZnFe₂O₄, ZnCr₂O₄, NiCr₂O₄), cation counterdiffusion was responsible for reaction. This difference in reaction mechanism for the similar systems studied in Lindner's work led to Carter's investigations which indicated cation counterdiffusion for the systems MgAl₂O₄ and MgFe₂O₄ [11]. A possible explanation of the discrepancies of previous marker-study experiments, namely the splitting of the chemically inert markers, was suggested by Carter.

The present studies indicate directly that the diffusion of Al³⁺ ions is involved in the solid-state reaction between Al₂O₃ and CuO. Although fig. 4a does not indicate clearly that the migration of Cu²⁺ ions also is involved in the reaction, consideration of the relative stabilities of the two reacting oxide phases would suggest that this is so. The absence of an orientation relationship between the aluminate and Al₂O₃ structures examined further disproves a reaction mechanism involving the diffusion of ions from one oxide layer into the more stable lattice of the other.
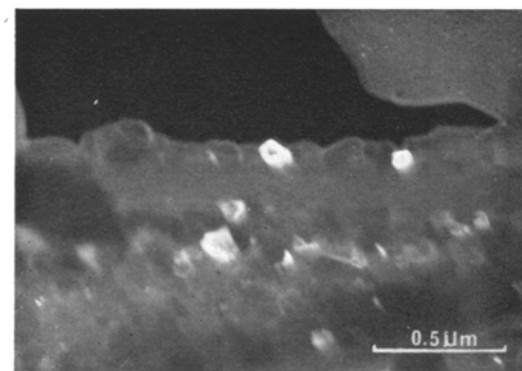
It was noted that there did appear to be some difference in particle size between the reacted and unreacted oxide regions. This would indicate surface diffusion of cations during reaction. After the initial formation of aluminate at the interface, further reaction would depend on the

(a)

(b)

(c)

Figure 4 An α-Al$_2$O$_3$:CuO thin film heated in air at 850° C for $2\frac{1}{4}$ h; (a) transmission electron micrograph showing original CuO particles nucleated and grown on the Al$_2$O$_3$ film edge. Particles have reacted to form CuAl$_2$O$_4$; (b) selected-area diffraction pattern from one of these particles (A); (c) dark-field micrograph of the diffracting particle. This sequence gives direct evidence for a cation counterdiffusion mechanism for the formation of the spinel phase.
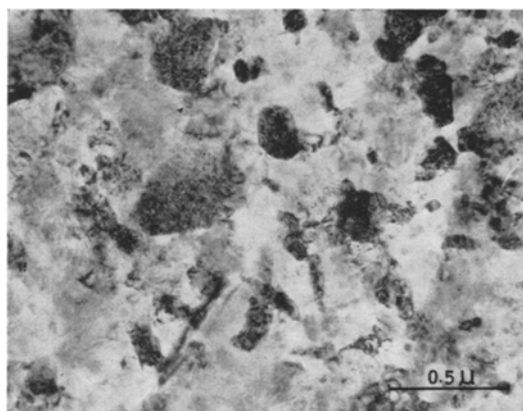

Figure 5 Transmission electron micrograph of an α-Al$_2$O$_3$: NiO film heated in air at 920° C for 75 h. Selected-area diffraction of this region indicated the presence of NiAl$_2$O$_4$. A defect-structure region is suggested by the observed contrast effects of the reacted zones.

diffusion of the reacting cations through or around this initial product layer. Migration of the ions around this layer by surface diffusion would obviously be easier, thus resulting in a variation in particle size and shape of the final aluminate regions from their original, metal-oxide particle shapes. Of course, it is possible that bulk diffusion of cations through the product layer also would have occurred. This bulk diffusion would have been facilitated by the presence of crystalline imperfections formed in the product phase during reaction. The observed contrast effects in the reacted regions for both the NiAl$_2$O$_4$ and CuAl$_2$O$_4$ suggest such an imperfect structure. Because of the fine size of the metal oxide particles studied in this work and because of the greater availability of oxygen ions for reaction with the migrating cations at the surface of these particles, it would appear reasonable that surface diffusion was the prominent mechanism of cation migration during the reaction.

5. Conclusions

The use of transmission electron microscopy for the investigation of the nature of the solid-state reaction between α-Al$_2$O$_3$ and CuO and NiO has been demonstrated. The observations indicate the formation of CuAl$_2$O$_4$ by a mechanism of cation counterdiffusion and reaction of the Al^{3+} and Cu^{2+} ions with O^{2-} ions at a free surface. Reaction was positively detected at temperatures as low as 710° C. Reaction of NiO and Al$_2$O$_3$ to form NiAl$_2$O$_4$ was observed at 910° C. The resultant aluminate regions for the

$CuAl_2O_4$ and $NiAl_2O_4$ appeared similar, a defect structure characterising these product layers.

Acknowledgements

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