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Metal/non-metal interfaces. The wetting of magnesium oxide by aluminium and other metals

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The sessile drop method has been applied to investigate interfacial effects that occur between single crystal MgO and molten Al, In, Ga, Sn and Au. For temperatures up to 1350 K the latter two metals do not wet MgO. The former three, however, form drops which expand along the surface with time. For the case of Al on MgO a well-defined reaction zone, having a chemical composition $MgAl_2O_4$ is formed. Aluminium vapour in contact with a hot MgO surface leads to the chemical etching of that surface, the reaction products being Mg and Al_2O.

1. Introduction

An understanding of those factors responsible for good adhesion between metals and ceramics is not only of scientific interest but also of considerable technological importance. The strength of interfaces in metal/ceramic composites or metal/non-metal seals depends critically on the ability of the metal to wet the other surface and a good deal of effort has been directed towards understanding the wetting process. Extensive studies have, for example, been carried out on alumina/metal systems, in particular using the sessile drop technique [1]. Gold adheres weakly to Al_2O_3 and molten drops make large obtuse contact angles with the surface [2]. Molten aluminium, on the other hand, at temperatures above 950° C wets the surface and also chemically reacts with it [2–4] to form volatile species and contact angles much less than 90°. Results described in the literature were confirmed in this laboratory for molten aluminium on etched sapphire surfaces. As part of a programme to investigate metal/ceramic interfaces these studies have been extended to the metal/MgO system. MgO has the advantage that atomically clean surfaces of high quality may be prepared with ease by vacuum cleavage or heating and that surfaces so prepared are now relatively well understood. Most of the studies described relate to the aluminium/MgO system but supporting data was also obtained for gold, tin, indium and gallium. The experiments have shown that in most of these systems the sessile drop technique is not applicable for detailed investigation of adhesion across the metal/MgO interfaces.

2. Experimental procedure

Experiments involving sessile drops were conducted in an ion pumped stainless steel ultra-high-vacuum system. The high temperatures necessary were obtained by radio frequency heating as shown in Fig. 1. The R.F. coil couples to a vertical cylindrical tantalum susceptor raising its temperature so that the MgO sample and metal drop are heated by its thermal radiation. Radiative losses were limited by a surrounding stainless steel shield slotted to prevent electromagnetic coupling to the induction coil. The sample, mounted on a ceramic platform, was located within the susceptor by a rack and pinion linear drive operable from outside the vacuum system. Observation of the profile of the sessile drop was possible through a window in the vacuum system and a series of 8 mm apertures in the susceptor and its radiation shield. The drops could be illuminated from the rear and photographed using a camera and telescope arrangement. Temperature was measured by means of an optical pyrometer.

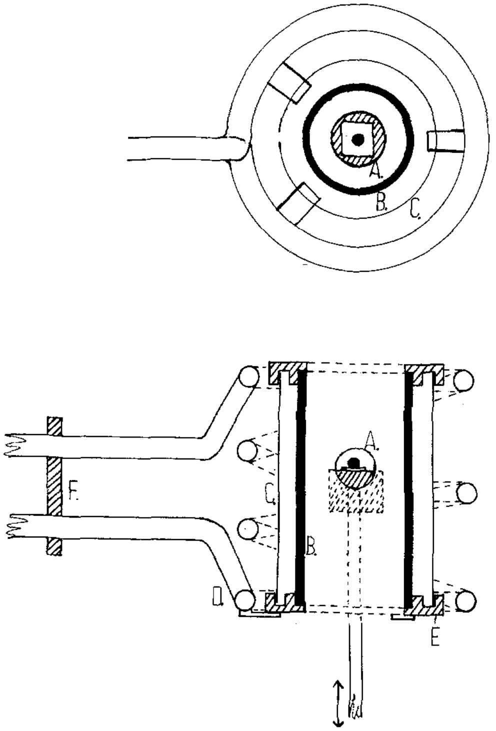

Figure 1 Plan and elevation of radio-frequency heated vacuum furnace. (A) Sessile drop on MgO substrate; mounted on ceramic stage. (B) Tantalum susceptor. (C) Slotted stainless steel reflector. (D) Water-cooled work coil. (E) Spacer/insulators, machined from "pyrophyllite" ceramic. (F) Dual insulated ultra-high-vacuum feedthroughs, water cooled.

Following these studies the samples were removed from the vacuum system and investigated further by optical microscopy, using an interference microscope. Chemical composition was investigated using a Cambridge "Geoscan" electron microprobe analyser. MgO crystals were obtained in the form of long bars from W. and C. Spicer Ltd. They were cleaved in the atmosphere into slices exposing (1 0 0) faces. At the temperatures, and vacua (10^{-9} to 10^{-8} Torr) involved in these experiments Auger electron spectroscopy established that the MgO surfaces were close to being atomically clean, prior to contact with the molten aluminium.

3. Results and discussion

3.1. Molten Al on MgO surfaces

The interaction of Al sessile drops with MgO surfaces was investigated in the range 1000 to 1350 K. Immediately upon contact with the hot surface the Al pellet formed a nearly spherical drop. However, the formation of an equilibrium contact angle was not observed. As far as could be seen, the only effect of increasing the temperature was to accelerate the expansion of the contact area. A series of photographs of the drop is shown in Fig. 2. Close examination shows a foot projecting from the base of the drop along the surface, at a temperature dependant rate, and the real contact angle, taken as the angle formed by the leading edge of this foot, is nearly zero. Thus, soon after melting, although the drop appears nearly spherical the real contact angle is not obtuse and wetting of the MgO surface has occurred. With time and expansion of the contact zone, the liquid metal formed a cap whose profile was a small segment of a sphere (Fig. 2). Associated with the development of the drop geometry was a constant reduction in the volume of the free liquid. Apart from simple evaporation of the drop at the liquid vacuum interfaces two other processes may be involved. The first is the reaction of aluminium with its oxide to yield volatile reaction products. The second is a diffusion effect across the liquid/solid interface. These are considered in subsequent sections.

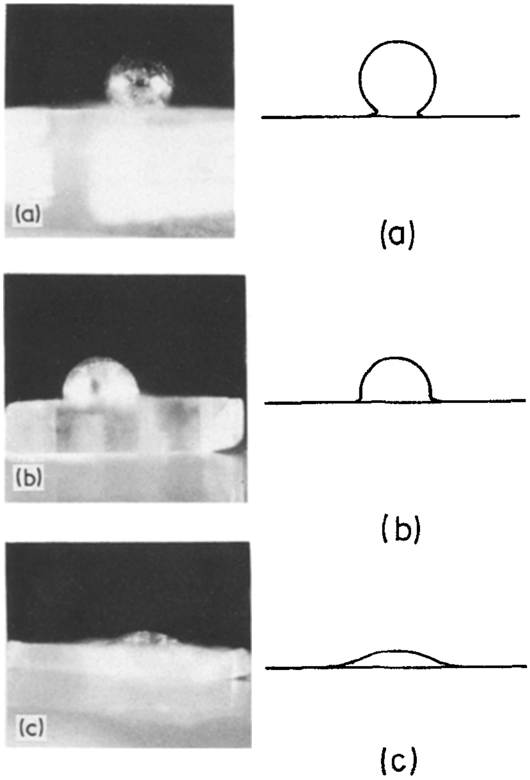

Figure 2 Photographs and diagrams of the form of an Al drop on a hot MgO surface with increasing time (a), (b), (c).

It is interesting to note that Al adheres strongly to MgO. Once a contact area was formed mechanical vibration did not displace the molten metal drop. Neither did adjacent drops coalesce to give a circular contact area, nor was molten Al ever observed to contract from a wetted area. This behaviour contrasts with that of gold drops on MgO as described later.

3.2. Optical microscope investigations

After cooling and removal from the ultra-high-vacuum system, samples were examined by optical microscopy. Three areas can be distinguished, as can be seen from Fig. 3. For this particular case, an Al pellet had been in contact with the MgO surface, at 1300 K, for 1 h. The central zone contains the metallic Al cap, whereas well away from the drop the surface is apparently etched, consisting of a high density of small rectangular pits, with sides parallel to the cleavage direction. Immediately outside the Al cap there exists an intermediate metallized layer projecting forward from the drop base. It is interesting to note that the movement of the front of this layer is highly anisotropic. The straight edges of the front make angles of 45° with the cleavage direction.

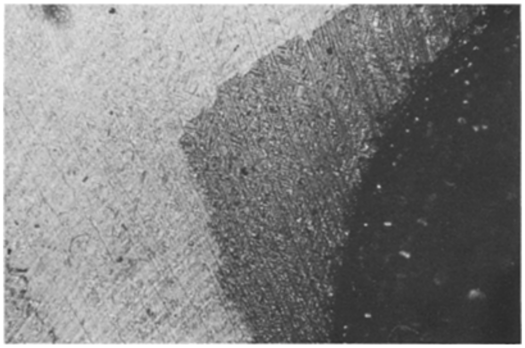

Figure 3 Photograph of MgO surface after an Al drop had been in contact with the surface for 1 h at 1300 K. The foot of the drop is the circular section on the right. Away from the Al drop the MgO surface has been etched. The intermediate zone displays the diffusion effects described in the text (X 45).

It is quite apparent that the Al vapour is responsible for the etching of the MgO surface. The etch pit density decreases with distance from the aluminium cap, and, in addition, areas such as the sides and back of the sample, not in direct line with the aluminium, are hardly affected. This is illustrated in Fig. 4.

Optical observations through the transparent MgO substrate showed clearly that a reaction had taken place between the Al drop and the MgO crystal. Sections taken through the crystal, following the dissolution of the Al cap in NaOH solution, showed a reaction zone extending to a depth of typically 100 μm below the Al. A typical section is shown in Fig. 5. The molten drop extended from the region labelled A towards the left of the crystal. Several points may be noted with regard to this reaction zone. Firstly, it is deepest beneath the centre of the Al cap and shallower towards the edge. However, a fairly deep zone also exists immediately below the periphery of the Al cap, and this zone is clearly visible in Fig. 5. Secondly, a reaction zone, indistinguishable from that in the central region, exists also beneath the intermediate zone of Fig. 3. This region is labelled AB in Fig. 5. Finally, the interfaces between the reaction zone and the unreacted MgO are sharp and in general seem to lie along (1 1 1) planes. The nature of this zone is considered further in Section 3.4.

It is concluded, therefore, that the parameters determining the geometry and properties of the

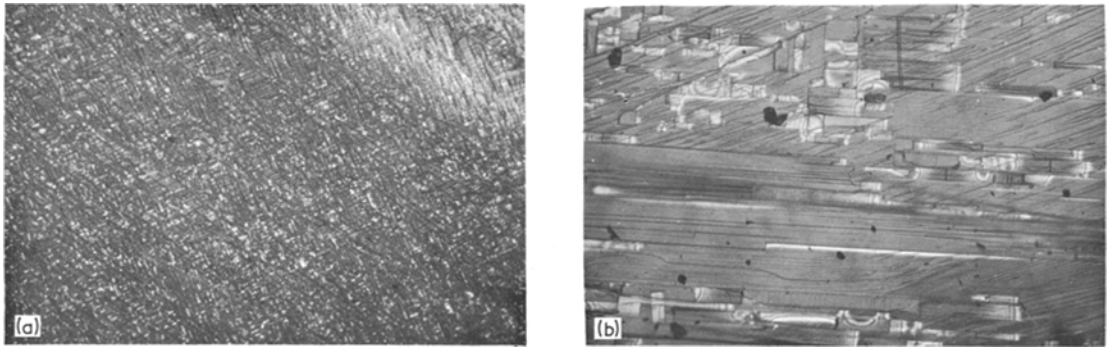

Figure 4 Micrograph of an MgO surface (b) after heating (a) after heating and exposing to Al vapour (X 45).

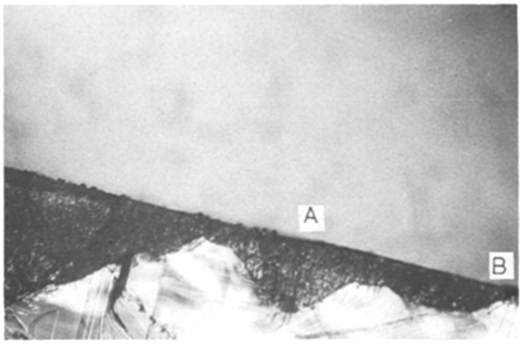

Figure 5 Micrograph of the reaction zone for an MgO crystal having been in contact with an Al drop. The drop has been dissolved off and the crystal cleaved to display a section through the reaction zone. The drop extended to point A and AB represents the intermediate zone discussed in the text (× 45).

interface of molten aluminium with MgO crystal are primarily chemical in origin and thus systematic observation of the contact angle is of little significance in establishing the adhesion of Al to MgO.

3.3. The vapour etching process

Before considering the nature of the reaction zone at the Al/MgO interface we first consider further the outer region of the crystal surface where vapour etching has taken place. The small, shallow pits resemble those usually observed in thermal etching processes [5].

One possibility is that the Al vapour reacts with the MgO surface to form a volatile suboxide such as Al_2O. The existence of this species, and its presence during the high temperature reaction of aluminium with refractory oxides was strongly indicated by early workers in this field [1, 3] and the thermodynamics of the process was considered. For MgO a possible reaction is

$$2Al + MgO \rightarrow Mg + Al_2O.$$

On the basis of published thermodynamic data [6] this reaction is not energetically favoured, being exothermic. However, it is favoured entropically and, of course, the reaction products are volatile.

In order to investigate this possibility further the reaction products were monitored using a Vacuum Generators Ltd 'Micromass 1' mass spectrometer. Aluminium vapour was deposited from a hot filament onto a heated MgO surface. The system was arranged in such a way that only the MgO crystal was in direct line with the admission aperture of the mass spectrometer. A species of mass 70, corresponding to Al_2O was indeed clearly detected when Al vapour was incident on the hot MgO surface. It was not, however, detected either if the MgO surface was not heated or if the MgO surface was heated in the absence of Al vapour. The presence of AlO was not observed and indeed it is not thermodynamically favoured – published results would not suggest its presence in concentrations greater than 0.1% of Al_2O [7]. As a result of the reaction involving the incident Al vapour, the MgO surface was etched, and the formation of volatile Al_2O and Mg account for the vapour etching process. Unfortunately the instrument did not enable Mg to be unambiguously detected from background components.

3.4. Composition of the reaction zone

After cooling to room temperature and removal from the vacuum system, the free aluminium was removed by dissolving in aqueous NaOH. The chemical compositions of the various zones were then investigated using the X-ray microanalyser. Two sets of samples were prepared by mounting in epoxy resin, grinding and polishing and the evaporation of carbon onto their surfaces. In one set the chemical composition along the MgO surface was monitored. In the other, the crystal was cleaved and the chemical composition of a section through the reaction layer (Fig. 5) examined.

For the outer etched region of Fig. 3, pure MgO was identified. Any Al present was in concentrations below the background level of the instrument (0.1%). However, both the central zone (from which the drop had been removed) and the intermediate zone of Fig. 3 gave results consistent with the presence of Al_2O_3, with only a small trace of Mg. This deposit, or surface layer, however, must be very thin as it could not be detected in the depth profile measured on the second set of samples.

The depth profile verified the presence of an intermediate oxide of fixed Mg/Al ratio, and the results were entirely consistent with that of the natural spinel $MgAl_2O_4$ [8]. The Mg/Al ratio was constant across the reaction zone and a typical depth profile is shown in Fig. 6. For the reaction

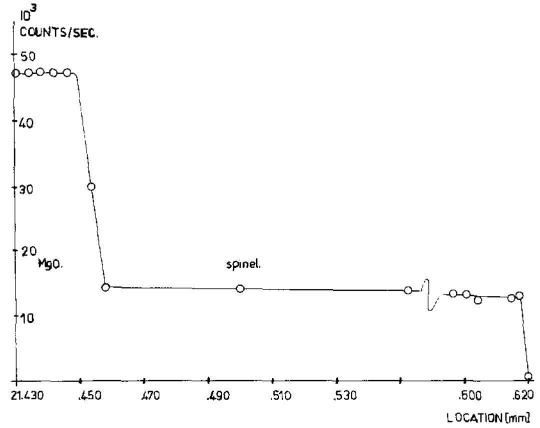

Figure 6 Geoscan microprobe concentration profile for Mg in a section through a substrate following the reaction of Al on MgO. Proceeding from the surface the count rate rises sharply (within 0.01 mm) from a value corresponding to the Mg content of spinel, $MgAl_2O_4$, to that of Mg in MgO.

to proceed Mg and Al species must diffuse across the reaction zone and the reaction must be relatively slow as determined by the inability to detect any concentration gradient of either species. It may be seen that the spinal component terminates abruptly with the proportion of Mg changing from that appropriate to spinel, to that appropriate to MgO, within 10 μm. Thus the rate of growth of the reaction zone is determined by the reaction at the metal/MgO or spinel/MgO interfaces and not by diffusion of metal species through the spinel. The fact that the spinel/MgO interface seems to favour some crystallographic planes (notably (1 1 1)) preferentially, would indicate that the interaction at this interface controls the reaction rate. It is interesting to note that the concentration profiles of the metallic components in the reaction zone are quite different from those described by Whitney and Stubican [9] for $MgO-Al_2O_3$ diffusion couples. However, the temperatures involved in those experiments were considerably higher than those encountered in the present studies.

Interesting also is the fact that the composition of the layer directly beneath the intermediate zone (AB in Fig. 5) is identical to that in the central region beneath the Al cap. This zone is produced predominantly by the diffusion of Al at or near the surface and subsequently into the bulk. The reason for the additional reactivity below the edge of the molten Al drop (below A in Fig. 5) is not clear but may be associated with the fact that Mg may be able to escape from the surface in this region.

These studies show, however, that the Al sessile drop, rather than being in contact with MgO, makes contact to a spinel $MgAl_2O_4$ reaction layer and the rate of expansion of the drop is determined by the rate of growth of this layer and yields no information relating to the adhesion of Al to MgO.

Finally, it was noticed that the spinel reaction zone grew at a considerably slower rate if the reaction proceeded in a vacuum of about 10^{-4} Torr. The reason is that the oxide layer surrounding the Al sphere is not removed at these pressures and the reaction is thus hindered. A similar effect has been observed for the reaction of Al with SiO_2 [10].

3.5. Other metals

In contrast to Al neither gold nor tin was found to wet MgO surfaces, for temperatures below 1350 K. Gold formed a nearly spherical droplet with contact angles approaching 180°. Likewise molten tin formed drops with large obtuse angles of around 130°, stabilizing at this value after about 1 h at 1250 K. The weak adhesion of these drops was easily observed by slight vibration of the sample, which caused both tin and gold drops to move freely on the surface. Furthermore, two gold drops, or two tin drops, on the same surface immediately coalesced upon contact, in contrast to the behaviour of Al on MgO. Upon cooling to room temperature the adhesion of gold and tin was found to be very weak compared to Al adhesion. Microscopic investigations showed no evidence of chemical reaction having taken place. Thus it is concluded that the failure of gold and tin effectively to wet MgO surfaces lies in their inability to react chemically with MgO.

Indium and gallium, on the other hand, behave in a manner similar to Al, but with very much slower reaction rates, at a given temperature. In both cases the expansion of the drop with time as well as the drop shape are determined by chemical rather than physical considerations. Although the chemical compositions of these reaction layers were not determined the products most probably are $MgGa_2O_4$ [11] and $MgIn_2O_4$.

Table I summarizes the results obtained for the various metals.

TABLE I Summary of the contact angles and adhesion of various molten metals on MgO single crystal surfaces.

Metal	Contact angle	Adhesion	Comments
Au	170°	Weak	No chemical reaction
Sn	130°	Weak	No chemical reaction
Al	Variable with time leading to wetting of the surface	Strong	Chemical reaction with the formation of spinel structures
In			
Ga			

4. Conclusions

(1) Molten aluminium, in the temperature range up to 1350 K, reacts chemically with MgO to form a spinel structure $MgAl_2O_4$. The growth of the spinel layer is controlled by the reaction at the spinel/MgO interface.

(2) The contact angle of molten Al drops on MgO is of little significance for establishing the adhesion of these two solids in contact.

(3) Aluminium vapour, in contact with a hot MgO surface leads to the formation of etch pits on that surface. The reaction products are metallic Mg and volatile Al_2O.

(4) Indium and gallium behave in a similar manner to Al but with very much reduced reaction rates. Molten gold and tin, however, do not wet, react with, or adhere strongly to MgO in the temperature range up to 1350 K.

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