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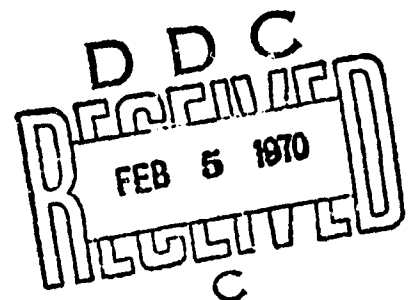
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INTERFACIALLY ACTIVE METALS IN METAL-CERAMIC COMPOSITES

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Metals Division

December 1969



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INTERFACIALLY ACTIVE METALS IN METAL-CERAMIC COMPOSITES

Technical Report by

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INTERFACIALLY ACTIVE METALS IN METAL-CERAMIC COMPOSITES

ABSTRACT

The role of the interface in metal-oxide composite materials has been investigated to determine the nature of bonding where an interfacially active metal has been used to promote wetting. A model system of Ag-MgO was used with titanium as the wetting agent. Electron diffraction was used to identify the magnesium titanate structure at the surface of the MgO crystal and the titanium oxides found in the adjacent titanium layer. Infiltration of the titanium oxide-magnesium titanate interface with liquid silver results in a separation of the solid oxide surfaces and the wetting and spreading of silver on the titanate surface. It is shown that the change in structure of the MgO surface must be taken into account when assessing the wetting phenomenon whenever an interfacially active metal is employed.

I. INTRODUCTION

Infiltration of metal oxide fibers by a metal can be easily accomplished if that metal is in a liquid state. However, if the product of this action is to be a composite wherein the metal is significantly strengthened by oxide fibers, then the following elements have been found necessary for the metal-metal oxide reaction:¹

1. An unbalance of surface energies to promote spreading of the liquid.
2. A bond between fiber and matrix capable of load transfer.
3. Bond stability over a wide temperature range.
4. Small interfacial reaction zones relative to the fiber diameter.
5. Close matching of thermal expansions of fiber and matrix.

Atomic bonds must be established, then, between the matrix metal and the oxide surface. If formation of those bonds brought about reduction of the oxide or creation of a new oxide phase at the expense of the original one, the useful size of the oxide fiber would be temperature dependent, violating at least two of the above recommended elements. Brush and Adams² and Sutton and Feingold³ have shown that such a situation can be avoided by providing a film of a second metal at the interface to promote wetting of the matrix metal and spreading without apparent damage to the oxide surface. In one case, several interfacially active metals have been found to be useful in brazing such difficult-to-wet materials as graphite, BeO, and Al₂O₃.⁴ On the other hand, some of the metals used as interfacial coatings are rather passive with respect to the oxide surface.³ These are deposited on the oxide by sputtering and immediately form bonds with the oxide surface. A liquid matrix metal then wets the coating, dissolving it to some extent. If dissolution is complete, dewetting of the oxide occurs, but if the coating is sufficiently thick, a "layered" composite is formed.

Only the first case, that of the "active" metal interfacial coatings, will be considered here, an active metal being one which will cause a permanent chemical change in the oxide surface structure and which is therefore not a true catalyst. Although the coating may be referred to as a metal coating, its actual makeup will be shown to be complex. A matrix metal in the liquid state can penetrate the active metal interfacial coating and "tunnel" between the coating and the oxide surface. A favorable interfacial energy relationship between the liquid and the coating has been assumed to be responsible for the observed capillary action. If the matrix metal does not wet the oxide surface in the classical sense,¹ a surface energy imbalance at the coating-liquid interface is assumed to overcome the disfavor and drag the liquid over the oxide surface.² Following the tunneling action, the interfacial coating is observed to break up somewhat and is either washed away by the liquid without dissolution, or it remains in place a short distance from the oxide surface completely surrounded by the matrix metal.

It is of interest to examine this interfacial coating and the wetting phenomenon since the coating is known to satisfy the established wetting criterion.

After wetting has occurred, the coating conveniently breaks away from the oxide surface, avoiding further reaction. Because its presence could seriously affect the strength of a composite, its nature should be determined. Further, anticipating that the coating would react in some way with the oxide surface, the resulting surface structure should be identified. Finally, some criteria should hopefully be established for the selection of oxide base, interfacial coating, and matrix metal by analysis of the wetting process and a determination of the products of the various reactions.

II. EXPERIMENTAL PROCEDURE

Well-characterized materials were chosen for the model system. The [100] faces of MgO single crystals were used as the substrate for ease of preparation of flat surfaces and to avoid grain boundary effects. No other planes were tried for comparison. Titanium (99.9%) is active in forming oxides, apparently a necessary characteristic trait for coating materials,^{2,4} and was therefore chosen as the active interfacial metal. Silver (99.9%) was selected for the wetting metal since the titanium-silver phase diagram is well known, showing some solubility of silver in titanium but very little of titanium in silver.⁵

An MgO single crystal of parallelepiped form was subjected to X-ray back reflection analysis to establish that the initially perpendicular external faces were, indeed, [100] surfaces. The crystal was then cut into wafers, approximately 19 mm x 9 mm x 0.8 mm. All cuts were made parallel to the external faces so that those surfaces on which the metals were deposited were of the [100] type. These crystal slices were washed in water, acetone, and methyl alcohol subsequent to cutting. For a wetting comparison test, all slices were half-masked and, at room temperature, in a vacuum of 10^{-5} mm Hg, exposed to a titanium vapor source emanating from a tungsten basket. Squares of silver foil, 0.25 mm thick and 1.5 mm on a side, were then placed on both the clean MgO surface and the titanium-coated surface of each substrate crystal. The assembly was mounted on the edges of a molybdenum foil boat, as shown in Figure 1, placed in a vacuum of 10^{-5} mm Hg, and heated by passing current through the foil. The temperature of the silver was raised to the melting point (960 C), held long enough for the liquid to assume its equilibrium shape on the substrate surface, and dropped by cutting off current to the boat.

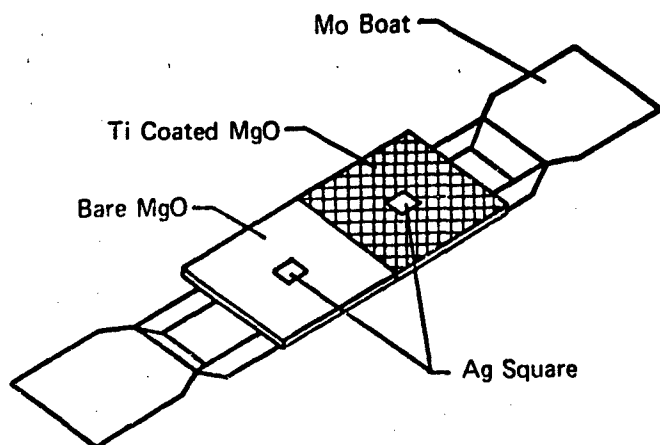


Figure 1. An MgO substrate, half coated with titanium and mounted on a molybdenum boat, prior to melting the silver.

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III. RESULTS AND DISCUSSION

Wetting and spreading of silver were found to be dependent on coating thickness. In general, coatings less than one micron thick did not allow wetting, i.e., all contact angles were greater than 90 degrees while coatings four microns thick permitted both wetting and spreading. Spreading occurred over large areas with low contact angles; but, as will be shown, these

contact angles are misleading. These observations, however, are consistent with previous work.^{2,4} All as-deposited coatings exhibited porosity, probably due to the rapid rate of deposition and the fact that the substrate was at ambient temperature. A thick interfacial coating could easily be broken into flakes after the substrate had been heated. The coating was brittle and adherence to the substrate was weak or nonexistent. If the coating was removed, the underlying substrate surface appeared textured. One flake of coating, shown in Figure 2, and its substrate surface counterpart were mounted separately for reflection electron diffraction in a Hitachi HU-11A electron microscope. Analysis of the substrate indicated that the predominant surface structure was the spinel, Mg_2TiO_4 . The flake consisted of TiO , TiO_2 , Ti , and at least one more unidentified substance, probably another titanium oxide.

Subsequent to the diffraction analysis, silver was melted on the uncovered substrate surface, and again on the clean MgO . As before, the contact angle for silver on MgO was high, $166^\circ 0'$; but the silver droplet on the surface found to contain magnesium titanate formed a contact angle of $89^\circ 55'$. Increasing the temperature beyond the melting point caused the silver to evaporate freely at a pressure of 10^{-5} mm Hg with no apparent change in the contact angle for either silver droplet.

No separation was directly observed between coating and substrate. Measuring the distance from the upper surface of a broken coating to the exposed adjacent substrate surface by an optical focusing technique gives the thickness of the coating plus any separation. Twenty-five readings taken at one break yielded a mean thickness of four microns with a standard deviation of two microns (see Table I). The flake shown in Figure 2, removed from the same specimen, varied from four to six microns thick by direct measurement of an electron beam shadowgraph. These numbers are not significantly different and, therefore, one cannot infer that a separation exists between coating and substrate. Tunneling of molten silver through the interface can be traced after solidification, however. The extent of lateral spreading under the coating, or tunnelling, can be seen with an optical microscope through cracks and pores in the coating where the upper surface of the coating has not been covered by silver. This distance is irregular and sometimes extends for several millimeters. Close to the planar edge of the silver spread on top of the interfacial coating, the silver which had tunneled under the coating returned to the upper surface through cracks and pores as in Figure 3.

Silver could be removed from the composite by reheating the substrate to 1000°C in a vacuum of less than 10^{-5} mm Hg, evaporating the silver, and leaving the coating in place. The coating surface was noticeably roughened after this evaporation, indicating some solubility of the coating in silver, but the coating remained brittle and could be broken into flakes as before. Again using the optical focusing technique, 25 measurements of the depth of this coating and any possible coating-substrate separation yielded the thickness values shown in Table I. Although a difference exists between the mean values, implying a coating-substrate separation of one micron, statistically the figures are not significantly different and no difference is claimed. Furthermore, any thickness change due to possible reaction of silver with the coating cannot be taken into account. What may be claimed is that paths by which the silver tunnels between coating and substrate are no more than one micron in depth. Earlier work indicated that the

penetrating liquid might break the coating and substrate apart as the liquid was drawn into the interface by capillary forces.⁴ The experiment reported here, however, showed that tunneling occurred across several millimeters without breaking the coating. Although the coating eventually breaks when enveloped by liquid, it is unlikely that the penetrating liquid forces crack extension.

The wetting process clearly involves complex reactions, and the bulk properties of the oxide substrate and the interfacial coating are in no way representative of their respective surface properties. An indication of the products expected by reaction of the interfacial coating and the oxide substrate at the melting point of the matrix metal can be obtained from the Gibbs free energies of formation of those compounds at that temperature.⁶ Assuming that titanium, its oxides, and MgO are the most likely reactants, Table II shows Mg_2TiO_4 to be the



Figure 2. Porous flake of interfacial coating material removed from the substrate surface. Mag. 46X



Figure 3. Photograph taken at the edge of the surface-silver (black, above) showing the tunneling silver (white) returning to the surface through cracks in the coating (gray, mottled). Mag. 150X

Table I. THICKNESS OF COATING AS MEASURED FROM THE SUBSTRATE SURFACE

	Number of Readings	Readings (in microns)			
		Low	High	Mean	Standard Deviation
Coating	25	3	9	4	± 2
Coating plus spacing (Ag evaporated)	25	4	10	5	± 2

Table II. FREE ENERGY OF FORMATION OF EXPECTED COMPOUNDS

Compound	$-\Delta G^0$ (1234 K)
TiO(B)	100,867 cal/mole
MgO	111,309
Mg_2TiO_4	402,050

most likely product. It is possible, however, that the reaction kinetics would prohibit formation of a thermodynamically predicted product within the time frame of the experiment.

Titanium picks up oxygen during evaporation and further complicates the state of the surface by reacting with the MgO. When the temperature is then raised to melt the silver, a thin interfacial coating presents a substantially oxidized surface to the molten silver. Silver does not readily react with MgO or the titanium oxides. High contact angles at the liquid-coating interface indicate an unfavorable surface energy relationship for wetting, so no spreading occurs in spite of the presence of pores in the coating. A thick coating, on the other hand, is rich in metallic titanium and is therefore easily wetted and its pores penetrated by silver. The extent to which silver attacks a thick coating by forming a solution with the titanium is evidenced by the roughening of the coating surface mentioned above.

After penetration of the coating has occurred, the situation changes markedly. An incoherent or perhaps discontinuous coating-substrate interface provides the path through which the molten metal is drawn. If capillary forces are responsible, their value is indicated by the contact angle of the liquid with each of the mating solid surfaces. For this reason the contact angle measured at the outer coating surface is misleading when wetting of the ceramic substrate is considered. The contact angle of silver on the ceramic substrate showed a considerable reduction after the formation of magnesium titanate at the magnesium oxide crystal surface. Contact angles measured from an MgO surface are therefore meaningless when titanium is introduced to the system. No sessile drop tests were performed on the substrate face of the coating as the coating fractured when removed. Without some knowledge of the wetting characteristics of that face one cannot say whether the substrate or the coating is responsible for the tunneling. If a coating substrate separation exists, however, the separation is small enough that substantial spreading will occur even at liquid-solid contact angles only slightly less than 90 degrees. The separation may not exist and in that event, the driving force for penetration is a reduction in energy of an incoherent boundary.

It is impossible to determine the proper intermediate active metal without consideration of the wetting metal or oxide base. In the case of a composite, however, the wetting or matrix metal and the oxide have usually been chosen for their physical properties and the remaining concern is for wetting promotion without violating any of the conditions previously established for the metal-metal oxide interface reaction. To accomplish this, the intermediate metal must diffuse into the oxide and form a structure which is stable relative to the structure of the supporting oxide, immune to corrosion by the matrix metal, and yet improves the wetting characteristics of the surface. Stability can be predicted from the Gibbs free energies of formation of the possible interfacial reaction products. After wetting has occurred, the coating should cease to be a source of metal ions for diffusion into the oxide. The weak interface is beneficial here in that it allows the liquid to break the coating away from the substrate. Electron diffraction has revealed that, in the case of titanium deposited on MgO, the coating is composed primarily of titanium oxides which are not reduced by silver. Whether or not the presence of titanium oxide particles in the matrix of a composite may be damaging to the strength of the system remains a question.

IV. CONCLUSIONS

When an active metal coating is used to promote the wetting of an oxide by a metal, the properties of the coating-oxide interface are not necessarily given by the corresponding surface properties of the coating or the oxide. Applying this to a silver-titanium-magnesium oxide composite, the following observations have been made:

1. Wetting of silver on a magnesium oxide substrate is improved by the formation of magnesium titanate on the substrate surface.
2. The titanium interfacial coating contains oxides which maintain stability in the presence of liquid silver.
3. A structural change at the substrate surface may be anticipated by minimizing the Gibbs free energy of formation for those compounds which can be created from the known constituents of the system.
4. Extensive spreading of a metal on an oxide can occur in the presence of an interfacially active coating although wetting, and therefore bonding, may be slight.

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