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Growth of intermetallic layers in the iridium–molybdenum system

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Abstract

Growth of intermetallic layers between molybdenum and an iridium alloy (Ir–0.3 wt.%W–0.006 wt.%Th–0.005 wt.%Al) has been evaluated over the temperature range 1473–1748 K, in argon and in vacuum. Two intermetallic layers, with compositions corresponding to IrMo and Ir_3Mo, are formed over the entire temperature range. The two layers have approximately equal thicknesses, and the total layer thickness formed during a 4 h exposure can be expressed as $t = 1200 \exp(-Q/RT)$, where t is the total thickness of the intermetallic layers in micrometers, $Q = 64$ kJ mol^{-1}, R is the gas constant, and T is the absolute temperature.

Vapor-phase transport of molybdenum (as MoO_3) is suggested as a possible mechanism for the growth of these intermetallic layers in (oxygen-contaminated) argon. There was no indication of molybdenum transport through the iridium alloy grain boundaries in advance of the intermetallic layer interface. The resistance of these intermetallics to attack by several acids and acid mixtures is similar to that of iridium.

1. Introduction

The Ir–Mo phase diagram [1] shows that four intermetallic phases can exist in the temperature range 1473–1748 K. The ordered IrMo phase with the orthorhombic B19 structure type has a narrow homogeneity range, reported as 50 ± 1 at.%, and the ordered Ir_3Mo phase with the hexagonal $D0_{19}$ structure type has a reported homogeneity range extending from 75 at.% Ir to about 66 at.% Ir at 1473 K [2]. The ϵ phase with a disordered h.c.p. structure has a large homogeneity range, as does the $IrMo_3$ phase with the cubic A15 structure type. A review of the literature revealed no information on the reaction kinetics of molybdenum and iridium.

The iridium alloy, Ir–0.3%W–0.006%Th–0.005%Al(wt.%), is used as fuel cladding in radioisotopic thermoelectric generators for space power systems [3]. During the processing of this material, it comes into contact with molybdenum at elevated temperatures. The purpose of this study was to determine the nature and the extent of the reaction between these materials over the temperature range of interest, as well as to develop methods to remove the reaction layers prior to further processing.

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2. Experimental details

The iridium alloy used in this study (Ir–0.3%W–0.006%Th–0.005%Al) was melted and rolled to produce sheets, and then surface ground to produce samples 0.6 mm thick. Diffusion couples were made in which an iridium-alloy sheet sample (metallographically polished through 600 grit SiC paper) was placed in contact on one side with commercially pure molybdenum sheet, which had been preoxidized in air at 773 K for 30 min, and on the other side with unoxidized molybdenum. The couples were placed in a container and compressed by means of a screw. The container and screw were made of Mo–0.5 wt.%Ti alloy. Each assembly was heated under an argon cover for 4 h. The test temperatures used were 1473, 1598, 1648, 1698, and 1748 K. A similar assembly, but with unoxidized molybdenum on both sides of the iridium alloy, was heated in a vacuum furnace at 1723 K for 4 h. After cooling, the containers were cut to expose the samples. It was observed that the molybdenum and iridium alloys did not adhere to each other after heating in argon but did adhere after heating in vacuum. In the case of the samples heated in argon, both the iridium and molybdenum surfaces were examined after they were separated, but intermetallic layers were found on only the iridium side of the diffusion couple. In the case of the vacuum sample, since the iridium alloy and molybdenum stuck together during the diffusion anneal, the composite assembly was polished and examined in cross-section without separating the iridium alloy from the molybdenum.

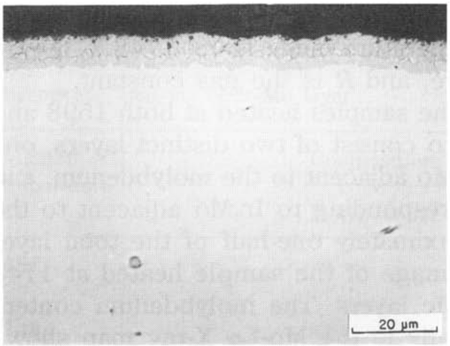
Measurements of intermetallic layer thicknesses were made using as-polished metallographic samples. The samples for optical metallography were etched electrolytically using an alternating current at a potential of 10 V, in a solution of one part HCl to four parts H_2O, with a small addition of NaCl for improved contrast.

X-ray microprobe analysis was performed on specimens cut from samples that had been heated at either 1598 or 1748 K for 4 h, and subsequently polished using standard metallographic practice. A JEOL 733 microprobe operated at 25 kV in the wavelength dispersive mode was used for this purpose.

Auger analysis was performed on the iridium alloy sample that had been heated at 1748 K for 4 h to determine whether any molybdenum had penetrated into its grain boundaries. The specimen was notched, cooled to approximately 170 K, and then impact fractured in the ultrahigh vacuum (1.5×10^{-8} Pa) of a high-resolution PHI 660 scanning Auger microprobe operated at 10 kV using beam currents of 0.5–2.0 μA. Depending on the size of the feature to be analyzed, the electron beam was either rastered over a given area or held stationary at a given location. Both intergranular and transgranular regions were analyzed to determine relative enrichments (if any) on the grain boundaries. The raw data were digitally smoothed and differentiated, and the relative peak height ratios from the differentiated spectra were used in our analysis.

3. Results

Optical micrographs of the intermetallic layers formed on the iridium alloy after 4 h in argon at 1598 and 1748 K are shown in Figs. 1 and 2 respectively. The total intermetallic layer thickness as a function of reciprocal temperature is shown in Fig. 3 for samples heated in argon at temperatures in the range 1473–1748 K. It should be noted that the average total layer thickness is similar for both the preoxidized and unoxidized molybdenum sides at temperatures of 1598 K and above. The layers were uniform in



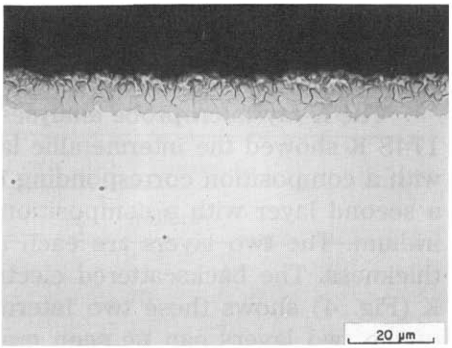


Fig. 1. Metallographic section of Ir–Mo diffusion couple showing that a layer of intermetallic compounds about 10 µm thick formed on the iridium alloy after 4 h in argon at 1598 K.

Fig. 2. Metallographic section of Ir–Mo diffusion couple showing that a layer of intermetallic compounds about 15 µm thick formed on the iridium alloy after 4 h in argon at 1598 K.

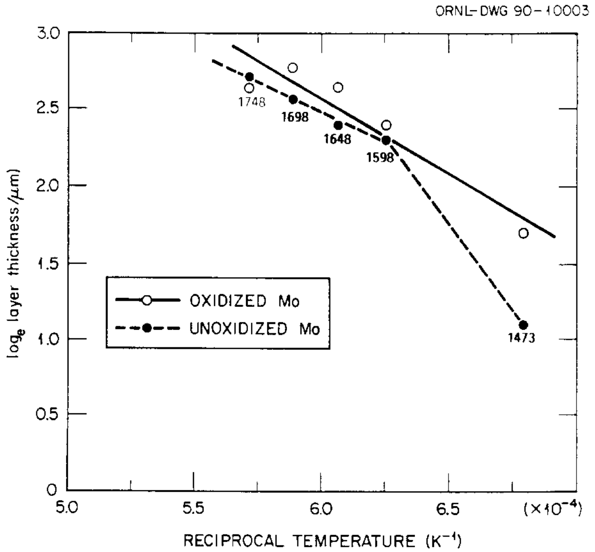


Fig. 3. Plot of intermetallic layer thickness as a function of reciprocal temperature for Ir–Mo diffusion couples heated for 4 h in argon.

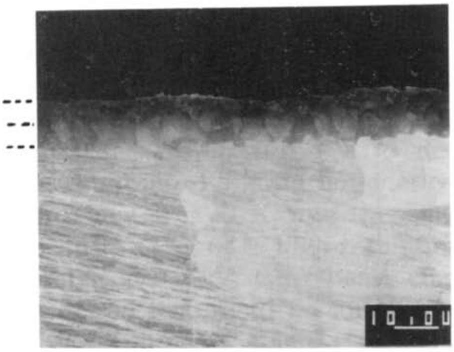
thickness to within 1 or 2 μm on each sample, and there were no areas on the sample surfaces that were not covered with the intermetallic layers. The sample heated in vacuum at 1723 K for 4 h exhibited a layer thickness of about 13 μm, although a number of areas of contact between the iridium alloy and molybdenum showed no intermetallic layer. At 1473 K, the intermetallic layer thickness is 4 μm on the iridium side in contact with oxidized molybdenum, and half that for the unoxidized molybdenum side. A least-squares fit to the data for unoxidized molybdenum in Fig. 3 gives a thickness of

$$t = 1200 \exp(-Q/RT),$$

where t is the total thickness (in micrometers) of the intermetallic layers formed during a 4 h exposure in the temperature range 1598–1748 K, $Q = 64$ kJ mol^{-1}, T is the absolute temperature, and R is the gas constant.

The X-ray microprobe analyses of the samples heated at both 1598 and 1748 K showed the intermetallic layer to consist of two distinct layers, one with a composition corresponding to IrMo adjacent to the molybdenum, and a second layer with a composition corresponding to Ir_3Mo adjacent to the iridium. The two layers are each approximately one-half of the total layer thickness. The backscattered electron image of the sample heated at 1748 K (Fig. 4) shows these two intermetallic layers. The molybdenum content of the two layers can be seen graphically in the Mo-Lα X-ray map shown in Fig. 5. Quantitative analyses of the layers are shown in Tables 1 and 2. Trace levels of tungsten (0.1 to 0.4 wt.%) were also found in the intermetallic layers, presumably resulting from the 0.3 wt.% tungsten content of the iridium alloy.

The fracture surface of the sample examined by Auger electron spectroscopy is shown in Fig. 6. It consists of two distinct regions: a fine-grained



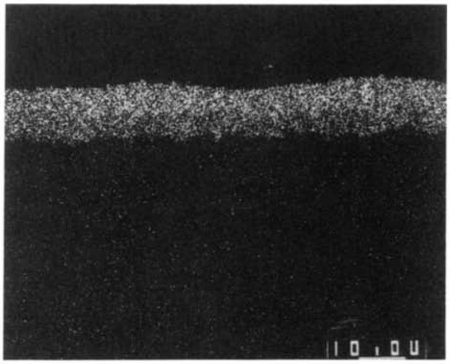


Fig. 4. Electron microprobe backscattered electron image of an Ir–Mo diffusion couple heated for 4 h at 1748 K showing intermetallic layers and grain structure of the intermetallic compounds.

Fig. 5. Electron microprobe Mo-Lα X-ray map of an Ir–Mo diffusion couple heated for 4 h at 1748 K showing two intermetallic layers, IrMo (light) and Ir_3Mo (medium grey).

TABLE 1

Microprobe analysis of IrMo layer

Reaction temperature (K)	Composition (at.%)	
	Molybdenum	Iridium
1598	48	52
	53	47
1748	52	48
	49	51

TABLE 2

Microprobe analysis of Ir_3Mo layer

Reaction temperature (K)	Composition (at.%)	
	Molybdenum	Iridium
1598	29	71
	27	73
1748	31	69
	33	67

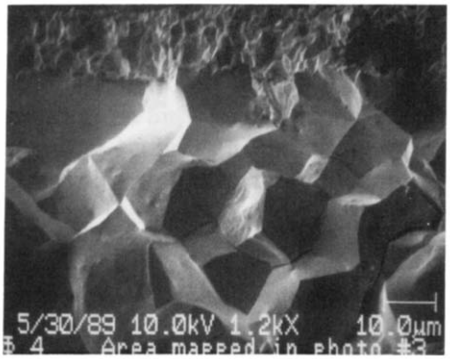


Fig. 6. Fracture surface of Ir–Mo diffusion couple heated for 4 h at 1748 K. The fine-grained region (top) is the intermetallic region and the coarse-grained region (bottom) is the iridium alloy.

surface region, which is actually composed of the two intermetallic layers described earlier, and a coarse-grained internal region, which is the iridium alloy. By its appearance alone it was not possible to deduce that the intermetallic region consisted of two different layers. However, as will be shown below, the molybdenum content decreased from the outer edge of the intermetallic layer to the inner edge, consistent with the outer layer being IrMo and the inner layer being Ir_3Mo. Fracture in the intermetallic region was essentially 100% intergranular, whereas in the underlying iridium alloy there were a few isolated transgranular cleavage regions scattered over the predominantly intergranular fracture surface.

Figure 7 shows representative low-energy Auger spectra from transgranular and intergranular regions in the iridium alloy, along with a couple from the intermetallic layer. Because the energies of many Auger transitions overlap, several peaks in these spectra can, in principle, be considered as belonging to more than one element, and have been labeled as such, even though some of the indicated elements may not actually be present. In order to determine whether an element is actually present, one has to consider peaks that do not overlap. Thus, the 186 eV molybdenum peaks in spectra (c) and (d) (which do not overlap with those of any other element in the alloy) show that molybdenum is present in the intermetallic region, but not in the iridium alloy. Similarly, the 65 eV thorium peak in spectrum (b) shows that thorium is present mainly on the grain boundaries of the iridium alloy. It is also present (in lesser amounts) in the intermetallic layer, but not in the transgranular regions (spectrum (a)). The ratio of the 186 eV molybdenum peak to the 54 eV iridium peak is considerably higher at the outer edge of the intermetallic layer (adjacent to the molybdenum) than at the inner edge

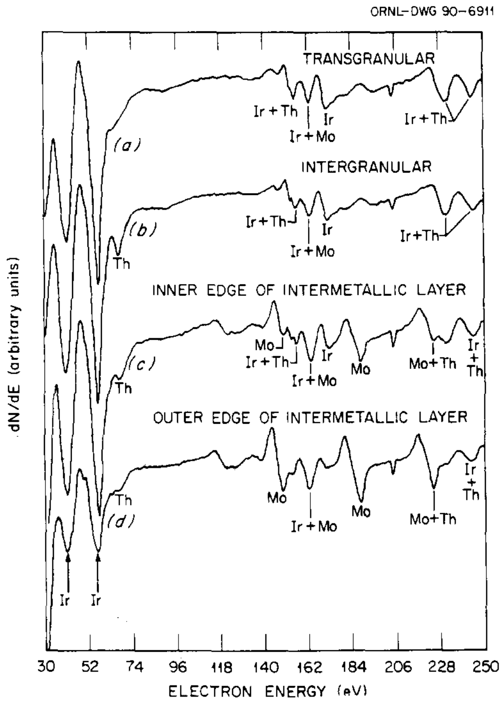


Fig. 7. Low-energy Auger spectra from (a) transgranular and (b) intergranular regions in the iridium alloy, and (c) inner edge and (d) outer edge of intermetallic layer.

(adjacent to the iridium), consistent with the outer layer being IrMo and the inner layer being Ir_3Mo as discussed earlier. However, quantification is not possible because of a lack of sensitivity data for Auger peak heights in intermetallics.

From both the X-ray microprobe and Auger data, it is clear that the iridium alloy reacts with molybdenum to form intermetallics at the interface. Another point of interest was whether there was any molybdenum penetration into the iridium grain boundaries during the diffusion anneal. Results for one grain boundary were discussed above, and we showed that there was no molybdenum present on that grain boundary. In excess of 20 additional grain boundaries were similarly analyzed at different locations in the iridium alloy, and molybdenum was not detected on any of them. We also performed spot analyses on a couple of iridium grain boundaries immediately adjacent to the intermetallic layer, and Fig. 8 shows the locations of two such spots on one grain boundary. These spots were at distances of 2.5 and 5 µm respectively from the interface. Molybdenum was not detected at either location, indicating that, even at distances as close as 2.5 µm to the interface, there was no molybdenum diffusion down the iridium grain boundaries.

The resistance of the intermetallics to chemicals was not studied in detail but, on the basis of limited results, appears very similar to iridium itself. The IrMo and Ir_3Mo intermetallic layers on the iridium alloy were examined metallographically after exposure to a variety of aggressive acid mixtures. There was no visible evidence of attack after 60 min in a mixture of 63 vol.% HCl (37%), 22 vol.% HNO_3 (70%) and 15 vol.% HF (48%) at room temperature, or in a mixture of 60 vol.% HCl (37%), 20 vol.% HF (48%), and 20 vol.% H_2O at 90 °C. However, the intermetallics are attacked by electrolytic cleaning with alternating current in a saturated aqueous KCN solution at an applied potential of 10 V, as is the iridium alloy itself. This cleaning technique has proven to be effective in production for complete removal of surface molybdenum contamination.

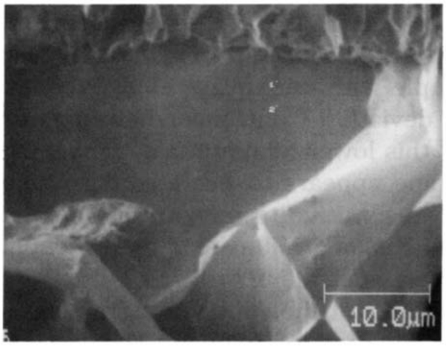


Fig. 8. Locations (1 and 2) of spot Auger analyses on iridium alloy grain boundary adjacent to the intermetallic layer.

4. Discussion

The analyzed compositions of the two intermetallic layers, IrMo and Ir_3Mo, are in reasonably good agreement with the Ir–Mo phase diagram. The absence of the $IrMo_3$ phase from the diffusion couple can be explained as the result of kinetic effects. An isothermal binary diffusion couple should, in principle, show all the phases which can exist between the end point compositions, with the relative thickness of each phase proportional to the square root of the diffusivity in the phase. The diffusion in the $IrMo_3$ phase may be sufficiently low that the width of this phase in the diffusion couple is too small to observe.

The formation of intermetallic compound layers requires that the molybdenum and iridium materials are either in intimate contact or that one of the two elements in transported through a gas phase to the opposite free surface. The results indicate that both of these mechanisms are observed under specific conditions. This is not surprising in that the temperatures are all above the boiling point of MoO_3, allowing oxide-vapor transport of the molybdenum to the surface of the iridium. Such an effect is clearly seen when the nonuniform thickness of the intermetallic layer formed in the diffusion couple heated in vacuum is compared with the uniform layer in the couple heated in (oxygen-contaminated) argon. The nonuniform layer thickness produced in vacuum is a result of imperfect contact between the polished (but microscopically rough) surfaces of the molybdenum and iridium alloy. In such situations, solid state reactions occur mainly at contact points between asperities on the mating surfaces. By contrast, in the presence of oxygen, the vapor transport of molybdenum produces a uniform intermetallic layer without the need for intimate contact.

The absence of any substantial difference in the intermetallic layer thickness between diffusion couples with oxidized and unoxidized molybdenum, for reaction temperatures in the range 1598–1748 K, indicates that intermetallic layer growth is not limited by transport of molybdenum to the iridium alloy surface. However, the factor of two difference at the 1473 K reaction temperature suggests that the supply of molybdenum at the iridium alloy surface may be the rate-limiting step for the couple with unoxidized molybdenum. This can also be seen as a sharp deviation from linear behavior in Fig. 3 at 1473 K for the diffusion couple with unoxidized molybdenum. The same plot indicates a much smaller deviation from linear behavior for the couple with oxidized molybdenum. At this lower temperature, the supply of molybdenum to the iridium alloy surface appears to be rate-controlling and the growth of the intermetallic layer is sensitive to oxygen availability. At the higher temperatures, the interdiffusion of iridium and molybdenum in the intermetallic layers is apparently rate-controlling.

One possible mechanism for the transport of molybdenum across gaps in the diffusion couple involves the participation of oxygen. The oxygen presumably oxidizes molybdenum, and the molybdenum oxide vapor is then transported to the outer surface of the intermetallic layer. At this surface, the molybdenum activity in the intermetallic is much lower than that of pure molybdenum and the molybdenum oxide is reduced, releasing the oxygen and providing molybdenum for additional layer growth. This mechanism is consistent with the observation that diffusion couples heated in the presence of oxygen exhibit an intermetallic layer which, upon release of the contact load, adheres only to the iridium alloy. In contrast, diffusion couples heated in vacuum exhibit an intermetallic layer which is tightly adherent to both sides of the couple.

5. Conclusions

The conclusions of this study of intermetallic layer growth in diffusion couples of molybdenum with an Ir–0.3%W–0.006%Th–0.005%Al alloy in the temperature range 1473–1748 K are as follows:

(1) Molybdenum reacts with the iridium alloy to produce two distinct intermetallic layers corresponding to the compositions IrMo and Ir_3Mo.

(2) Intermetallic layer growth occurs by interdiffusion of iridium and molybdenum through the intermetallic layer. No indication of molybdenum transport through the iridium alloy grain boundaries in advance of the intermetallic layer interface could be found.

(3) Vapor phase transport of molybdenum across gaps in the diffusion couple produces intermetallic layers of uniform thickness when the reaction occurs in the presence of oxygen.

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