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THE USE OF DIFFUSION BARRIERS IN REDUCING METAL-METAL INTERACTIONS AT 1100 °C

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ABSTRACT

In fabricating an isotope heat source, design considerations frequently dictate the use of multiple layer of dissimilar metals to contain the fuel. At high temperatures, interdiffusion between the dissimilar metals can endanger the integrity of the source. The use of diffusion barriers is one way of reducing or eliminating the interdiffusion reactions. Aluminum oxide films represent a logical choice for a diffusion barrier. Boron silicide was also suggested as a potential barrier material. In this study both materials were evaluated as diffusion barriers at 1100 °C with a variety of metal-metal couples.

Aluminum oxide appeared to effectively reduce metal-metal interaction as compared to couples in which no diffusion barrier was present. Boron silicide, on the other hand, apparently was ineffective in reducing the interaction. In some cases it appeared to increase interaction. Based on the results obtained with Al_2O_3, a more detailed study on its use as a diffusion barrier appears warranted.

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THE USE OF DIFFUSION BARRIERS IN REDUCING METAL-METAL INTERACTIONS AT 1100 °C

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INTRODUCTION

In fabricating an isotope heat source, design considerations frequently dictate the use of multilayers of dissimilar metals or alloys to contain the isotope fuel form. If the source is intended for high temperature use, reactions between the dissimilar metal layers can endanger the integrity of the source. These reactions can cause embrittlement or even failure of a layer or liner during long-term use. Reactions between the stainless steels or superalloys and the refractory or noble metals appear to be especially bad in this regard.

Previous work at this laboratory[1] has identified many of the metal-metal couples which are subject to severe interdiffusion reactions at 1100 °C. Since it is highly desirable to use some of these same metal-metal composites in constructing certain isotope heat sources, methods of reducing the interaction must be found. The use of diffusion barriers to reduce or eliminate interdiffusion is the obvious answer. However, finding suitable diffusion barriers which will be effective, and retain their integrity during the construction and operation of the heat source is a difficult problem.

In selecting materials for testing as diffusion barriers, oxide films are a logical choice. They can be applied in thin dense adherent layers and should serve to reduce diffusion, if they are non-reactive with the substrates. Aluminum oxide was selected as the best of the oxide materials to be evaluated as a diffusion barrier.

It was suggested that boron silicide (B_6Si) might also be effective as a diffusion barrier, especially if the outer surface of the silicide layer was oxidized to form a thin oxide glaze prior to use. The silicide can be deposited as a dense adherent film on most substrates by flame spraying. Therefore, it too was evaluated as a diffusion barrier in this work.

Other compounds should also be evaluated as potential barriers, but program funds did not permit a more detailed study. This report summarizes the results obtained with aluminum oxide and boron silicide diffusion barriers and a variety of metal-metal couples.

SUMMARY

The effectiveness of B_6Si and Al_2O_3 as barriers in reducing the diffusion between metal-metal couples at 1100 °C has been investigated. Couples studied included those of 304L stainless steel, Hastelloy X and Hastelloy C with rhenium, W/26 Re, tantalum, tungsten and TZM. The tests were carried out for 1000 and 4000 hr.

Aluminum oxide appeared to effectively reduce metal-metal interaction as compared to couples in which no diffusion barrier was present. Boron silicide, on the other hand, apparently was ineffective in reducing the interaction. In some cases it appeared to increase interaction.

Based on the results obtained with Al_2O_3, a more detailed study on its use as a diffusion barrier appears warranted.

EXPERIMENTAL

The construction of isotope heat sources generally calls for at least a two layer clad: the outer layer being an oxidation resistant material, while the inner layer must be compatible with the isotope fuel form. In many cases, a refractory metal, one of its alloys, or rhenium makes up the inner layer, while one of the stainless steels or superalloys make up the outer protective layer. Therefore, how these layers of materials will interact at elevated temperatures is vital to the design of an isotope heat source. Three different outer layer materials were used in this study: 304L SS as representative of the stainless steels, Haynes 25 as representative of the cobalt base superalloys and Hastelloy X as representative of the nickel base superalloys.

The couples of these materials which were studied included:

304L SS	-	Tantalum
304L SS	-	Tungsten
304L SS	-	W/26 Re
304L SS	-	Rhenium
304L SS	-	TZM
Haynes 25	-	Tantalum
Haynes 25	-	Tungsten
Haynes 25	-	W/26 Re
Haynes 25	-	Rhenium
Haynes 25	-	TZM
Hastelloy X	-	Tantalum
Hastelloy X	-	Tungsten
Hastelloy X	-	W/26 Re
Hastelloy X	-	Rhenium
Hastelloy X	-	TZM

Two different diffusion barrier materials, boron silicide and aluminum oxide, were evaluated with each couple.

COUPLE PREPARATION

The couples used in these studies were prepared from bar stock and metal sheet or foil. The 304L SS, Haynes 25, and Hastelloy X portions of each couple were machined from bar stock, normally 1.5 in. diameter hot-rolled rod. The tantalum, tungsten, W/26 Re, rhenium, and TZM portions of each couple were made from metal sheet or foil. The diffusion barrier materials were applied to the sheet or foil by flame spraying. Each piece of metal which had been coated with B_6Si was oxidized at 1000 °C for 1 min to form a thin oxide glaze on the B_6Si surface.

With 304L SS as an example (Figure 1), the following procedure was used in preparing the test couples. A capsule was machined from 1.5 in. diameter 304L SS rod. A plug of 304L SS with machined faces was placed into the capsule (slip-fit). A piece of clad metal (i.e., Ta, W, etc.) with the diffusion barrier on each face was placed on top of the metal plug. The thickness of the clad metal varied from 5 to 15 mils depending on the metal. A second plug of 304L SS was then inserted, followed by a second clad metal specimen. This sandwich-type construction was continued until all five clad metals (with diffusion barriers) were in place. A cap of 304L SS was then pressed in place and the capsule sealed by electron beam welding. After welding, the capsule was pneumatically impacted[2,3] to improve the surface contact between the various layers. A similar procedure was used in preparing the Haynes 25 and Hastelloy X couples.

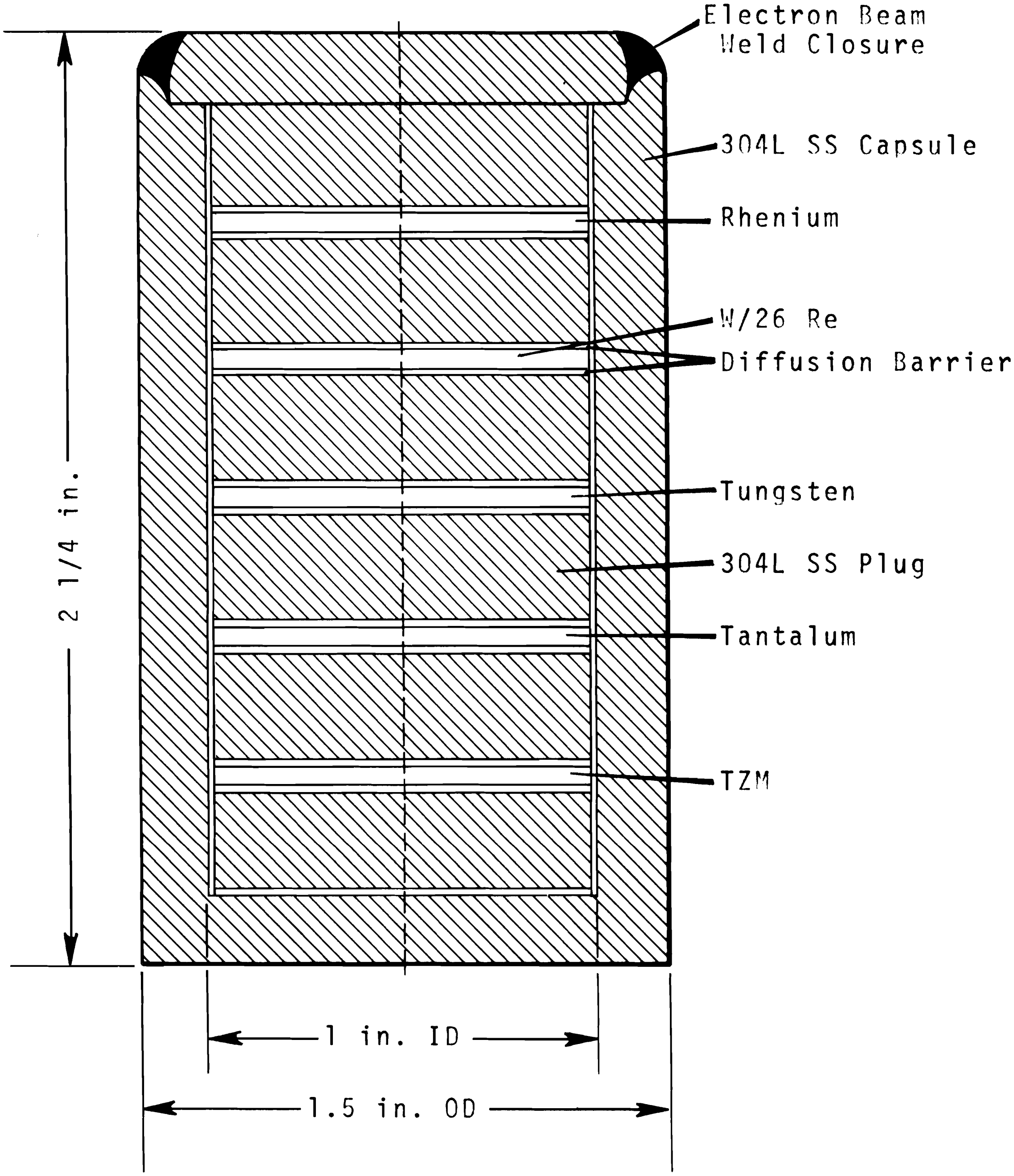


FIGURE 1. Cross Section of Test Capsule

As a control, similar capsules to those described above were prepared without the diffusion barriers between the dissimilar metal layers, and were tested concurrently with the couples containing the diffusion barriers.

Each capsule was sealed in an Inconel 600 envelope to protect the outer surface of the capsule from air oxidation at the test temperature.

TEST CONDITIONS AND COUPLE EVALUATION

The tests were carried out in a muffle furnace at 1100 °C. Temperature of the furnace was maintained within ±10 °C of the control point. The couples were tested for 1000 and 4000 hr.

At the conclusion of the test, the couples were cooled and the Inconel 600 protective envelopes removed. Each capsule was examined manually for external oxidation. Each capsule was sectioned vertically, into quadrants with an abrasive saw. One quadrant of the capsule was mounted for polishing and metallographic examination. The interdiffusion zone of each couple was determined from both photomicrographs and electron microprobe scans.

When the couples having aluminum oxide diffusion barriers were examined, it was impossible to retain the Al_2O_3 surface during the polishing and etching operation. The oxide washed away, leaving a void space between the two dissimilar metals. This made estimation of the extent of interaction more difficult.

RESULTS AND DISCUSSION

Capsules that had been pneumatically impacted, but not tested at temperature, were examined to see what affect impaction had on the various couples. Microscopic examination showed no interaction between dissimilar metals when a diffusion barrier was not present. Where B_6Si was present, there was a very thin reaction zone (less than 0.1 mil) between the flame sprayed silicide and the metal substrate. It was no thicker, however, than for the B_6Si coated metal which had not been pneumatically impacted. The silicide film did not appear to be physically damaged by impaction. The same comments apply to the Al_2O_3 containing couples. In summary, therefore, it does not appear that pneumatic impaction caused any measurable interaction between the dissimilar metal and diffusion barriers.

The metal-metal diffusion observed in the control couples without diffusion barriers is summarized in Table 1. The values presented are the average of the diffusion zone thicknesses of the two faces of each clad metal specimen. Typical photomicrographs of the metal-metal interfaces are shown in Figure 2. The diffusion zones measured for 304L SS and Hastelloy X couples are generally somewhat less than those reported previously.[1]

The data obtained with the control couples serve as a basis for judging the effectiveness of the diffusion barriers.

When boron silicide is present as a diffusion barrier, the reactions that occur at the interface are quite complex. Examination of the couples indicate little reaction between the dissimilar metals. However, there are extensive reactions between

TABLE 1. Diffusion in Control Couples at 1100 °C[(a)]

Couple Composition	Approximate Diffusion Zone Thickness, mils 1000 hr	4000 hr
304L - Rhenium	1	3
304L - W/26 Re	1	2
304L - Tungsten	1	2
304L - Tantalum	1	3
304L - TZM	1	4
Hastelloy X - Rhenium	<1	2
Hastelloy X - W/26 Re	<1	2
Hastelloy X - Tungsten	<1	2
Hastelloy X - Tantalum	2	5
Hastelloy X - TZM	<1	1
Haynes 25 - Rhenium	1	2
Haynes 25 - W/26 Re	1	2
Haynes 25 - Tungsten	<1	1
Haynes 25 - Tantalum	2	3
Haynes 25 - TZM	1	2

(a) As determined from photomicrographs and electron microprobe analyses.

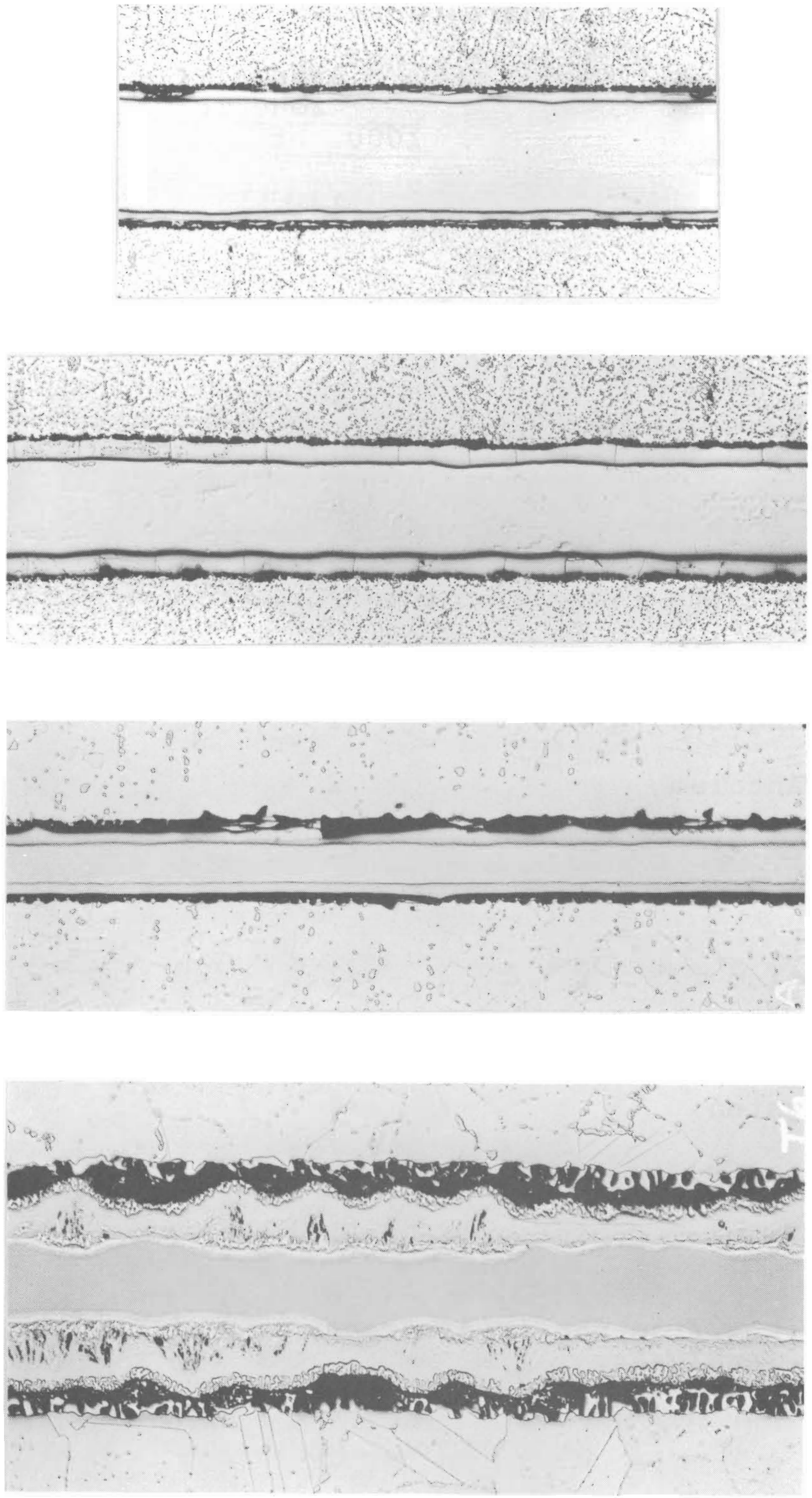


FIGURE 2. Diffusion in Control Couples at 1100 °C

the metals and the boron silicide. In Table 2 is summarized the data for the B_6Si containing couples. The extent of the interaction zone was estimated from the thickness of clad metal that was unaffected for each couple. On a comparative basis, the clad metal appears to react as rapidly when the B_6Si is present as when it is not. In some cases, the rate of reaction appears to increase. Typical photomicrographs of silicide containing couples are shown in Figure 3.

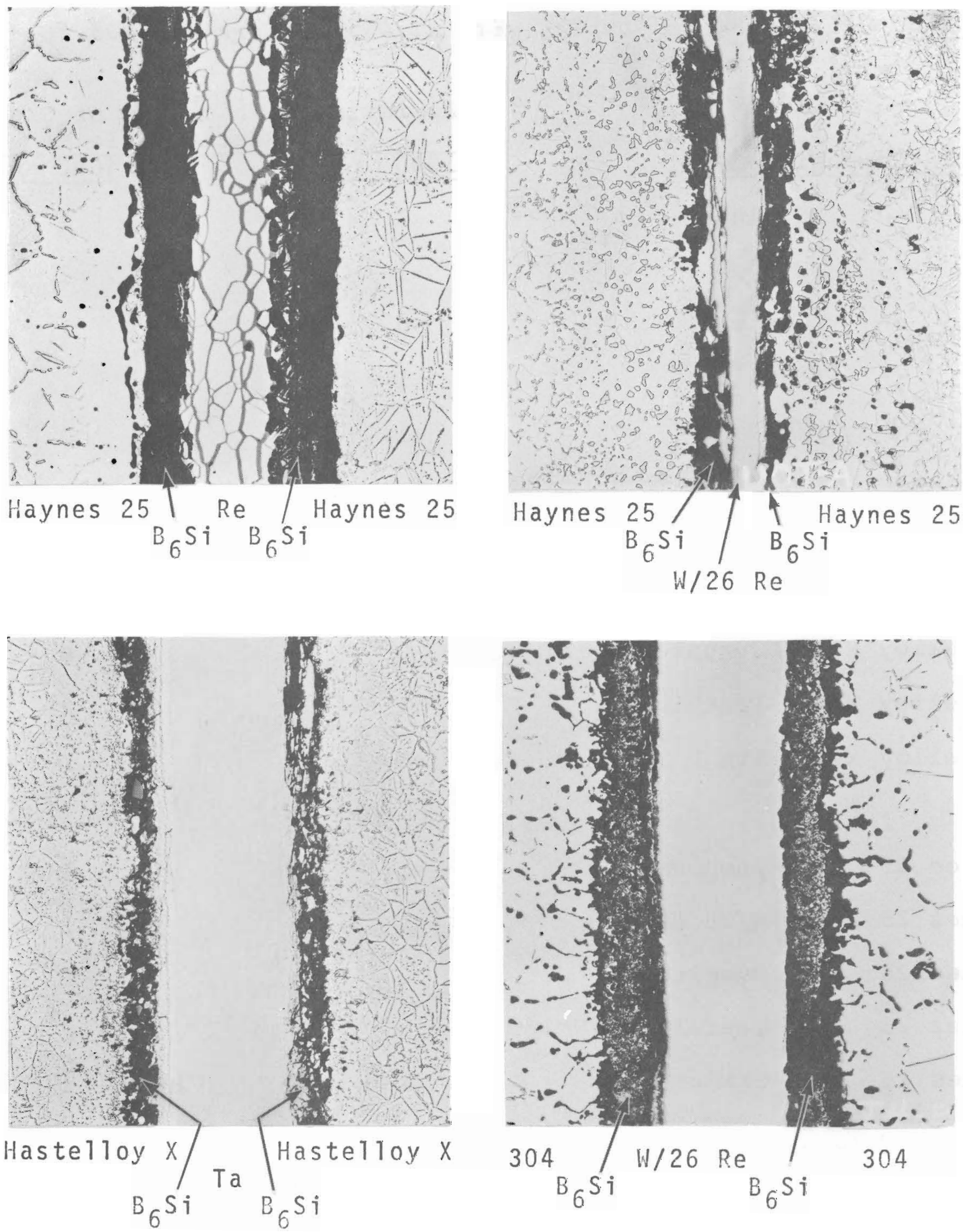
Data for the aluminum oxide containing couples are given in Table 3. Again, the extent of clad metal interaction was estimated from the thickness of unaffected metal. Al_2O_3 definitely appears to have reduced the extent of interactions of the couples under consideration. An exact measure of the interaction is difficult because of the void space created by the loss of Al_2O_3 during polishing and etching. However, the data present should be accurate within 20 to 30% of the actual values. Photomicrographs of various Al_2O_3 containing couples are shown in Figure 4.

In carrying out these studies, the only intent was to obtain a measure of the effectiveness of the diffusion barriers. No attempt was made to determine the actual mechanisms of the interaction under consideration. Those desiring more information on the actual mechanisms of the metal-metal interactions are referred to Reference 1.

TABLE 2. Diffusion in Couples with Boron Silicide Barriers at 1100 °C.

Couple Composition	Approximate Thickness of Clad Metal Reacted, mils[a] 1000 hr	4000 hr
304L - Rhenium	1	3
304L - W/26 Re	1	3
304L - Tungsten	2	4
304L - Tantalum	2	3
Hastelloy X - Rhenium	1.0	2
Hastelloy X - W/26 Re	1.5	2
Hastelloy X - Tungsten	2.5	3
Hastelloy X - Tantalum	2.5	4
Haynes 25 - Rhenium	1.5	3
Haynes 25 - W/26 Re	1.5	2.5
Haynes 25 - Tungsten	2	3
Haynes 25 - Tantalum	2	3

(a) *As determined from photomicrographs and electron microprobe analyses.*



<u>FIGURE 3.</u> *Diffusion in Metal-Metal Couples at 1100 °C with B_6Si Barriers Present (4000 hr, 100X)*

TABLE 3. Diffusion in Couples with Al_2O_3 Barriers at 1100 °C

Couple Composition	Approximate Thickness of Clad Metal Reacted, mils[a] 1000 hr	4000 hr
304L - Rhenium	<1	1
304L - W/26 Re	<1	<1
304L - Tungsten	0	1
304I - Tantalum	1	1
304L - TZM	<1	2
Hastelloy X - Rhenium	0	<1
Hastelloy X - W/26 Re	<1	<1
Hastelloy X - Tungsten	0	0
Hastelloy X - Tantalum	1	2
Hastelloy X - TZM	<1	1
Haynes 25 - Rhenium	<1	1
Haynes 25 - W/26 Re	<1	1
Haynes 25 - Tungsten	0	<1
Haynes 25 - Tantalum	0	2
Haynes 25 - TZM	1	2

(a) *As determined from photomicrographs and electron microprobe analyses.*

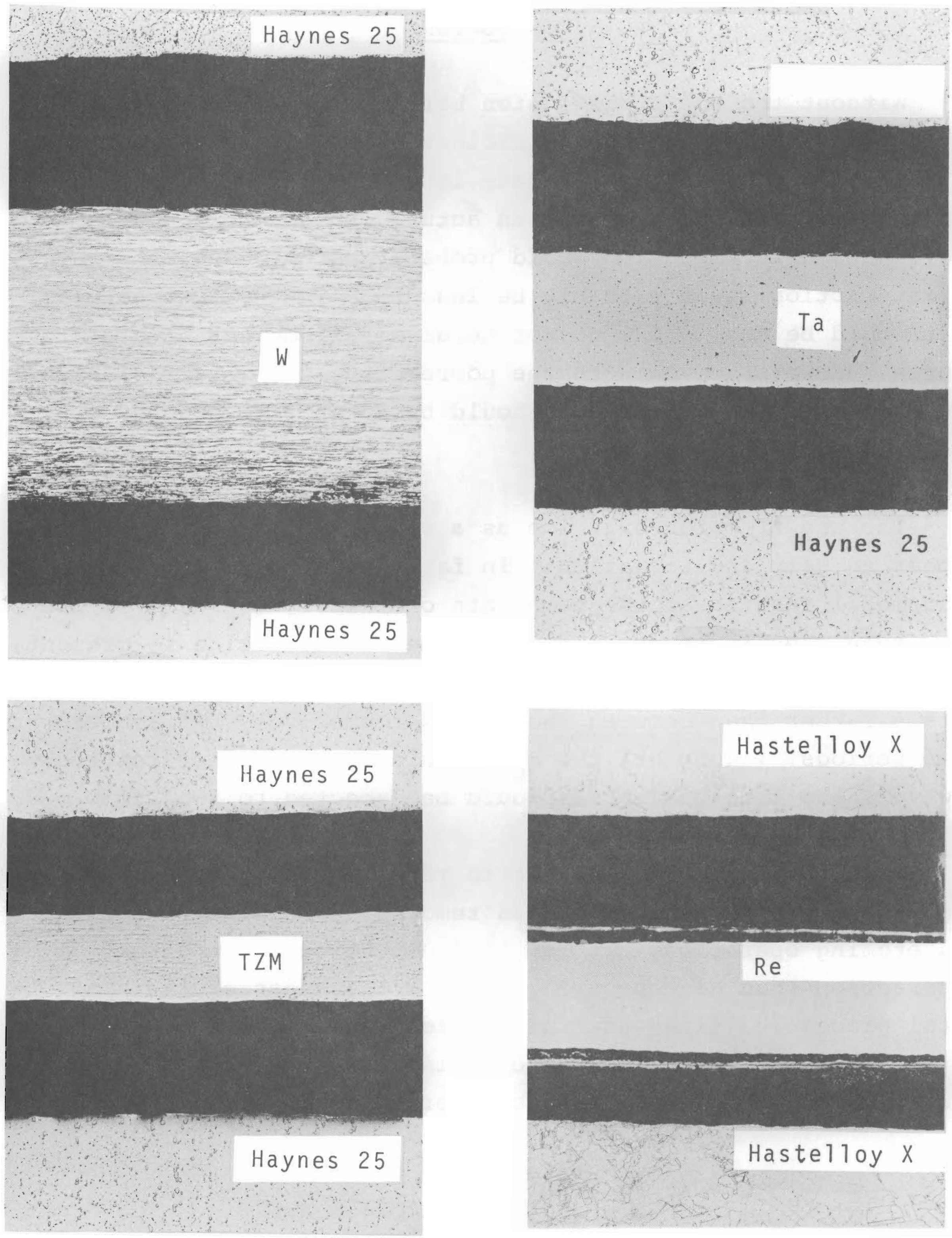


FIGURE 4. *Diffusion in Metal-Metal Couples at 1100 °C with Al_2O_3 Barriers Present (4000 hr, 100X)*

CONCLUSIONS

Without the use of diffusion barriers, all of the metal-metal couples studied show sufficient interaction at 1100 °C to raise doubt as to the ultimate integrity of the couple over extended periods of time. In an actual isotope heat source, where pneumatic impaction would probably not be used, the rate of interaction would probably be less than in the test couples. This would be due to the poorer metal-metal contact in a heat source. However, even with the poorer contact, interdiffusion would still be a problem and should be taken into account in the design of the source.

The use of boron silicide as a diffusion barrier does not appear to help the situation. In fact the data show that the clad metal reacted at the same rate or faster when B_6Si is present than when it isn't. However, when the silicide is present, the reaction appeared to be between silicide and the individual metals rather than between the metals themselves. At longer time periods, (>4000 hr) the B_6Si would be completely reacted, however, and then the metals would be expected to interact.

Aluminum oxide does appear to reduce the interaction between the metals. Since the Al_2O_3 was removed during the polishing and etching operations, it is difficult to tell the extent of interaction that had occurred, but the thickness of the clad metal pieces indicates the interaction was decreased as compared to the control samples. A more definitive study of the use of aluminum oxide as a diffusion barrier appears warranted.

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