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REACTION OF SELECTED METAL-METAL COUPLES AT 1100 °C

L. J. KIRBY
H. T. FULLAM

JUNE, 1967

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By

L. J. Kirby
H. T. Fullam

Chemical Research Section
Chemistry Department

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TABLE OF CONTENTS

LIST OF FIGURES

REACTIONS OF SELECTED METAL-METAL COUPLES AT 1100 °C

L. J. Kirby and H. T. Fullam

INTRODUCTION

Frequently the integrity of multi-layered isotopic fuel capsules, fabricated for high temperature use, is endangered by metal-metal reactions between dissimilar metals and alloys. These reactions can cause embrittlement or even failure of a liner during long-term use. This behavior points out an urgent need which exists for the characterization and evaluation of these metal-metal reactions. This report summarizes the results of preliminary studies of a number of metal-metal couples.

SUMMARY

Metal-metal couples were studied after exposures up to 4000 hr at 1100 °C to characterize and evaluate the reactions which occurred. The couples studied included:

- Hastelloy X
  - rhenium
  - molybdenum/50 rhenium
  - tungsten/25 rhenium
  - tungsten
  - tantalum
- Tantalum
  - rhenium
  - tungsten/25 rhenium
  - tungsten
- 304L SS
  - rhenium
  - tungsten/25 rhenium
  - molybdenum/50 rhenium
  - tantalum
  - iridium
  - platinum
- Rhenium
  - molybdenum/50 rhenium
  - tungsten/25 rhenium
  - platinum
- Platinum
  - tungsten/25 rhenium

In addition, the reactions of Hastelloy X and Hastelloy C with rhenium, tungsten/25 rhenium, and tantalum were studied following experiments where the temperature was cycled (700 to 1100 °C).

Hastelloy X and 304L SS reacted with rhenium, molybdenum/50 rhenium, and tungsten/25 rhenium to form diffusion zones where there was little tendency for the individual metals in Hastelloy X or 304L SS to migrate preferentially. The diffusion zone appeared to approach a limiting thickness in long term tests of the 304L-rhenium couple. In reactions between Hastelloy X or 304L SS and tantalum, nickel tended to concentrate at the tantalum-rich side of the diffusion zone. Iron showed a finite but lesser tendency to concentrate at the

tantalum-rich side, while chromium showed no tendency toward this preferential migration.

Tantalum reacted very slightly with rhenium, tungsten/25 rhenium, and tungsten. Platinum reacted extensively with rhenium and tungsten/25 rhenium, and was totally unacceptable as a liner for 304L SS capsules. Iridium behaved similarly with 304L SS. Hastelloy C, studied only in temperature cycling tests with rhenium, tungsten/25 rhenium, and tantalum, was slightly less reactive than Hastelloy X. When compared with the static tests, the diffusion reactions were generally more pronounced for temperature cycling tests with Hastelloy X.

RESULTS AND DISCUSSION

The metals and alloys that were studied fall into two groups. The first group contained rhenium and rhenium alloys, tantalum, tungsten, platinum, and iridium. The second group contained the alloys Hastelloy X and 304L SS and might also include other alloys such as Haynes-25, Inconel, etc., which have not yet been studied.

EXPERIMENTAL PROCEDURES

Couples of Hastelloy X, Hastelloy C, and tantalum with other metals and alloys were prepared from metal rods and foils. In a typical example (Figure 1), a shallow Hastelloy X capsule was machined, four layers of 0.003 in. rhenium were inserted, a Hastelloy X plug was then pressed tightly into place and the capsule was electron beam welded closed. Tantalum capsules were prepared in a similar manner. For the temperature cycling tests, Hastelloy X capsules were machined, metal foils inserted, a Hastelloy C plug was pressed in place and electron beam welded. After welding, all capsules were pneumatically impacted to assure intimate contact between the test metals, and were then sealed in evacuated quartz envelopes prior to being placed in the furnace.

Reactions between the couples rhenium-molybdenum/50 rhenium, rhenium-tungsten/25 rhenium, platinum-rhenium, and platinum-tungsten/25 rhenium were evaluated from multilayered capsules. For example, a capsule was assembled by stacking foils of rhenium, platinum, rhenium, tungsten/25 rhenium, platinum, tungsten/25 rhenium, rhenium, and Hastelloy X (primarily as a filler) in a rhenium-lined 304L SS capsule. Similarly, rhenium and molybdenum/50 rhenium were layered in a Hastelloy X capsule. The capsules were electron beam welded, pneumatically impacted, and sealed in

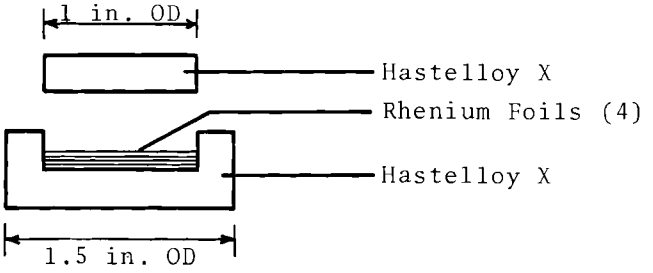


FIGURE 1. Hastelloy X-Rhenium Couple

evacuated quartz tubes. In all cases, sufficient layers of each metal foil were used to eliminate any masking effect that might arise from an adjacent metal.

Reactions of 304L SS with various liner metals were studied by examination of metal-lined test capsules. 304L SS capsules were lined with a metal foil (rhenium, tungsten/25 rhenium, molybdenum/50 rhenium, tantalum, iridium, or platinum), filled by cold-pressing the capsule contents into place, electron beam welded closed, and pneumatically impacted. The capsules were sealed in evacuated quartz envelopes for in-furnace protection. The cross section of a typical capsule is illustrated by Figure 2.

In other experiments, the effect of volatility of 304L SS was tested on several foils. Loose foils of rhenium, molybdenum/50 rhenium, or tantalum were sealed in evacuated 304L SS capsules, and the capsules were then sealed in evacuated quartz envelopes.

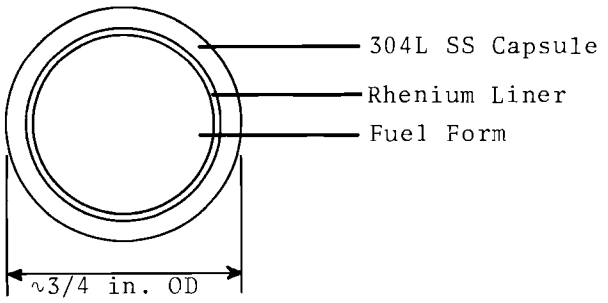


FIGURE 2. Rhenium-Lined 304L SS Capsule

Evaluations of the metal-metal reactions and loose metal foils were made from metallographic and electron microprobe analyses. Each capsule was sectioned with an abrasive saw, and a portion mounted for polishing and examination. After polishing, typical reaction cross sections of the test capsules and metal specimens were examined and measured. The diffusion zones were measured from both the photomicrographs and the electron microprobe scans, but the scans provided more precise measurements, and were used for final evaluation of the reactions.

STATIC TESTS OF METAL-METAL COUPLES

The metal-metal reactions observed from static tests at 1100 °C (except for the couples with 304L SS, which are discussed separately) are summarized in Table I. Typical photomicrographs of the metal-metal couples after heating are presented in Figures 3 and 4. The microprobe traces of Hastelloy X couples with rhenium, molybdenum/50 rhenium, tungsten/25 rhenium, and tungsten showed similar patterns for the distributions of the individual metals across the diffusion zones. Examination revealed a sharp decrease in each Hastelloy X alloy component measured at the edge of the diffusion zone adjoining the Hastelloy X. Generally, the individual metals reached sloping plateaus in their concentrations in the diffusion zone and decreased rather sharply to zero at the edge of the unreacted rhenium, molybdenum/50 rhenium, tungsten/25 rhenium, or tungsten; the liner

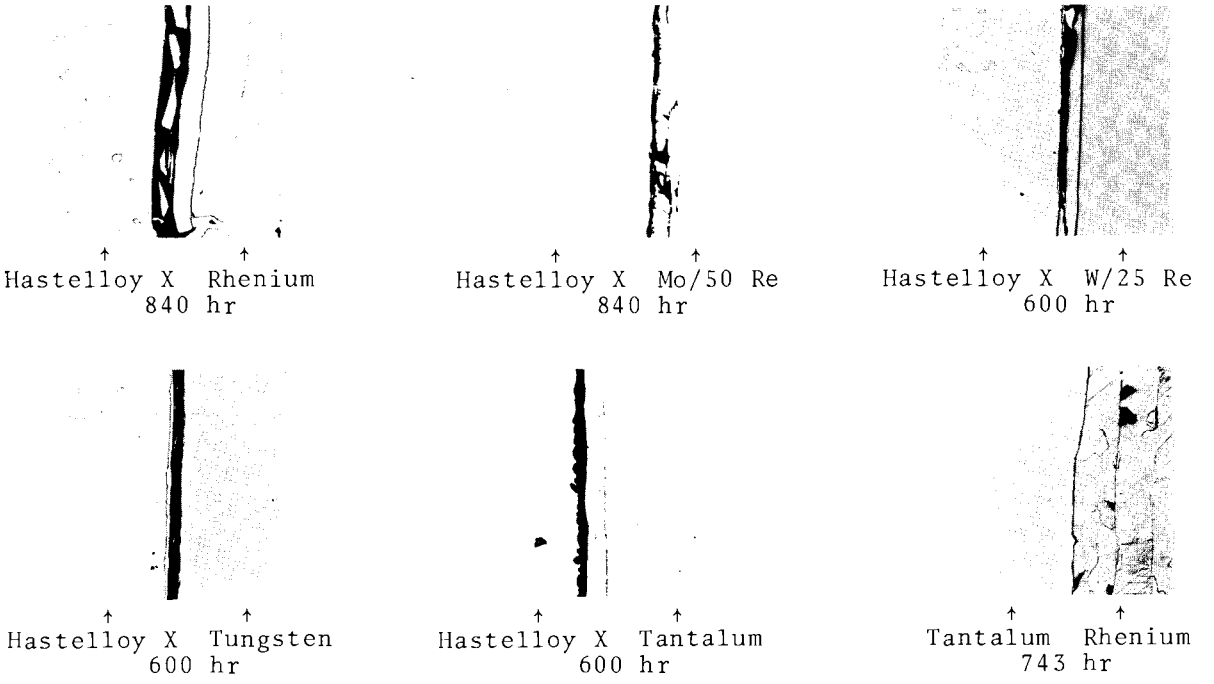


FIGURE 3. Photomicrographs of Metal-Metal Couples Heated at 1100 °C

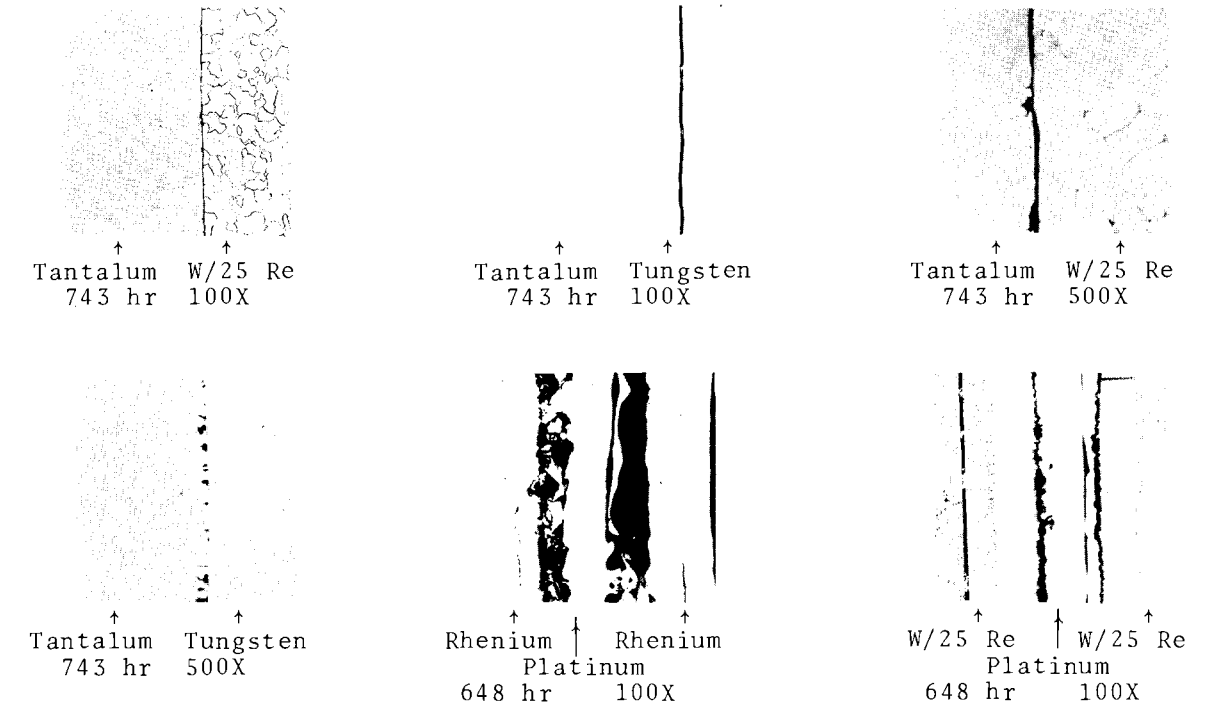


FIGURE 4. Photomicrographs of Metal-Metal Couples Heated at 1100 °C

TABLE I. Metal-Metal Reactions at 1100 °C

Metal Couple	Hours at 1100 °C	Approximate Diff. Zone Thickness, in.	Remarks
Hastelloy X-Re	840	0.0015	"Holes" in rhenium appear due to pneumatic impaction. Actual metallic interactions are slight. No preferential diffusion of Hastelloy X components.
Hastelloy X-Mo/50 Re	840	0.0015	No preferential diffusion of Hastelloy X components.
Hastelloy X-W/25 Re	600	0.001	No preferential diffusion of Hastelloy X components.
Hastelloy X-W	600	0.0005	Very slight diffusion at Hastelloy X-tungsten interface. No preferential diffusion of Hastelloy X components.
Hastelloy X-Ta	600 840	0.0025 0.003-5	Three or more separate layers in diffusion zone. Nickel appears to move preferentially through the tantalum, concentrating ahead of the Hastelloy X components on the tantalum-rich side. Iron may also do this, to a smaller extent.
Ta-Re	743	0.0004	"Holes" in rhenium appear due to pneumatic impaction. Very slight diffusion at tantalum-rhenium interface.
Ta-W/25 Re	743	~0	No diffusion at interfaces during tests.
Ta-W	743	~0	No diffusion at interfaces during tests.
Re-Mo/50 Re	840	~0	No diffusion at interfaces during tests.
Re-W/25 Re	648	~0	No diffusion at interfaces during tests.
Pt-Re Pt-W/25 Re	648 648		Platinum integrity rapidly destroyed. Not determined whether rhenium or W/25 Re, or O_2 traces are responsible for the effects observed. W/25 Re somewhat less reactive than rhenium.

metals tended to mirror this effect. Typical metal distributions for the Hastelloy X-rhenium couple, normalized from the electron microprobe traces, are shown in Figure 5. Distributions of the elements across the diffusion zones with molybdenum/50 rhenium, tungsten/25 rhenium, and tungsten showed similar patterns. Examination of the photomicrographs usually revealed the presence of a void space between the diffusion zone and the Hastelloy X, shown on the traces as a sharp initial dip to zero for the nickel, iron, and chromium.

The Hastelloy X-tantalum couple reacted in a more complex manner

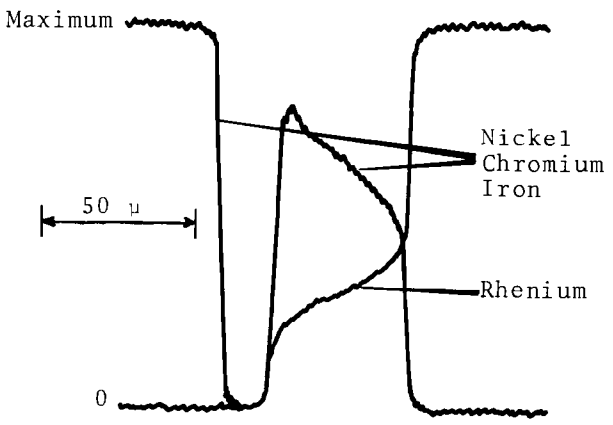


FIGURE 5. Metal Distributions for Hastelloy X-Rhenium Couple (600 hr at 1100 °C)

(Figure 6). A layered diffusion zone formed between the test metals and the electron microprobe traces revealed a definite tendency for nickel to concentrate at the tantalum-rich side of the diffusion zone. Iron also showed this tendency, but to a lesser extent than nickel. The metal concentrations varied substantially from layer to layer across the diffusion zone, possibly indicating a tendency toward the formation of a number of intermetallic compounds with tantalum. The presence of a void space, probably formed during the cooling period after the test couples were removed from the furnace, was also evident at the left of the nickel, iron and chromium traces.

Other reactions of tantalum during the relatively short test times recorded were very slight. In the cases of tantalum-tungsten/25 rhenium and tantalum-tungsten, a very slight reaction zone was noted at only one side of the foil layer. The minimal reaction noted, (Figure 4) may have been caused by improper cleaning or assembly of the test couples, or by entrapment of traces of air during capsule preparation. This reaction needs to be rechecked.

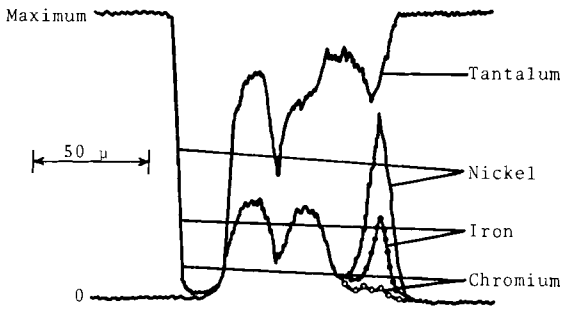


FIGURE 6. Metal Distributions for Hastelloy X-Tantalum Couple (600 hr at 1100 °C)

Platinum reacted very extensively with rhenium. The tungsten/25 rhenium alloy was somewhat less reactive with platinum, but it is obvious from examination of the photomicrographs (bottom of Figure 4) that platinum would not be a suitable liner or outside container for either of these metals. As will be shown later, this high reactivity of platinum was also noted with 304L SS, as well as with the samarium sesquioxide fuel form stand-in.

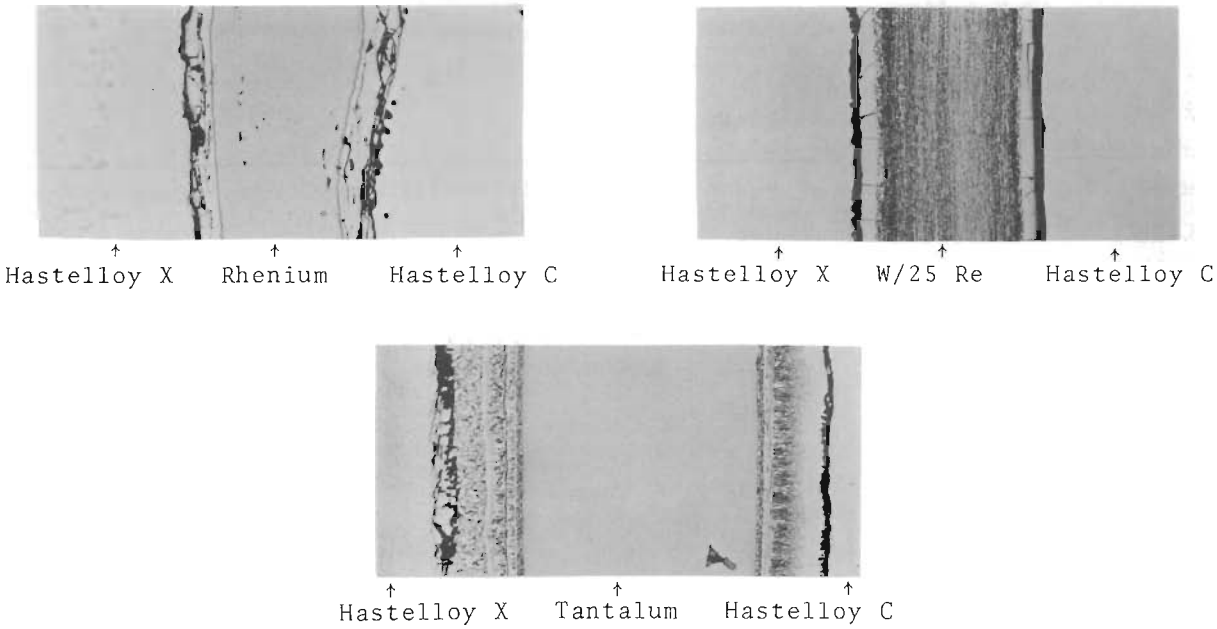
TEMPERATURE CYCLING TESTS OF METAL-METAL COUPLES

Reactions with Hastelloy X and Hastelloy C from temperature cycling tests at 700 to 1100 °C are summarized in Table II. Comparison of the data in Tables I and II for the reactions of Hastelloy X with rhenium, tungsten/25 rhenium, and tantalum demonstrates vividly the effect of temperature cycling, which may complicate capsule design problems. Must less time was required to produce the same thickness diffusion zone when the temperature was cycled. Photomicrographs of the metal-metal couples after the temperature cycling tests are presented in Figure 7. Although the reactions proceeded much farther with temperature cycling, the distributions of the various metals across the diffusion zones followed the same general patterns (Figures 5 and 6). The step-like diffusion zones were observed for the Hastelloy X or C-rhenium and Hastelloy X or C-tungsten/25 rhenium couples. There was no preferential diffusion of a Hastelloy X or Hastelloy C component through rhenium or tungsten/25 rhenium. Layering of the diffusion

TABLE II. Metal-Metal Reactions with Temperature Cycling

Metal Couple	Total hr 700 °C*	Total hr 1100 °C*	Approximate Diff. Zone Thickness, in.	Remarks
Hastelloy X-Re	130	223.5	0.002	"Holes" in rhenium appear due to pneumatic impaction. Metallic interactions are small, but more noticeable than for static tests. No preferential diffusion of Hastelloy X or Hastelloy C components.
Hastelloy X-Re	126.5	306.5	0.002	
Hastelloy C-Re	130	223.5	0.002	
Hastelloy C-Re	126.5	306.5	0.002	
Hastelloy X-W/25 Re	144.5	308.5	0.0015	Metallic interactions more noticeable than for static tests. No preferential diffusion of Hastelloy X or Hastelloy C components.
Hastelloy X-W/25 Re	142.5	212.5	0.0015	
Hastelloy C-W/25 Re	144.5	308.5	0.001	
Hastelloy C-W/25 Re	142.5	212.5	0.001	
Hastelloy X-Ta	179.5	290.5	0.006	There were at least six distinct layers in the diffusion zone. Nickel appears to move preferentially through the tantalum, concentrating ahead of other Hastelloy X or Hastelloy C components on the tantalum-rich side. Iron may also do this, to a smaller extent.
Hastelloy X-Ta	161.5	266.5	0.0065	
Hastelloy C-Ta	179.5	290.5	0.006	
Hastelloy C-Ta	161.5	266.5	0.0055	

**Frequency of cycling approximately 24 hr*



100X

FIGURE 7. Photomicrographs of Metal-Metal Couples Cycled at 700 to 1100 °C

zones for the Hastelloy X or C-tantalum couples was greatly accentuated, however, and the electron microprobe traces revealed up to six distinct peaks compared with three for the static temperature test (Figure 6). Again, nickel and iron tended to concentrate at the tantalum-rich sides of the diffusion zones.

METAL-METAL REACTIONS IN LAYERED CAPSULES

Reactions with 304L SS from static tests at 1100 °C are summarized in Table III. Some of the data for the 304L SS-rhenium reaction, plotted in Figure 8, illustrate that the diffusion zone for this couple tends to approach a limiting thickness in long-term reactions. Photomicrographs of typical metal-metal couples after heat treatments are presented in Figure 9.

Comparison of the photomicrographs in Figure 9 with those for the Hastelloy X couples (Figures 3 and 4, page 4) shows that similar reactions are occuring for the two alloys with various potential liners. The electron microprobe traces revealed that there was no tendency for preferential diffusion of any 304L SS component in the couples of 304L SS with rhenium, molybdenum/50 rhenium, tungsten/25 rhenium, iridium or platinum. Nickel and iron concentrated slightly at the tantalum-rich side of the 304L SS-tantalum couple. Iridium reacted with the 304L SS components in a uniform but extensive manner, and platinum reacted rather destructively with the 304L SS. It is certain that platinum could not be used to line 304L SS capsules for high temperature use, and iridium should probably not be considered without very extensive testing to assess the effects of the reaction

TABLE III. Metal-Metal Reactions at 1100 °C

Metal Couple	Hours at 1100 °C	Approximate Diff. Zone Thickness, in.	Remarks
304L-Re	840	0.002	No preferential diffusion of any 304L SS component.
304L-Re	1576	0.0035	
304L-Re	2184	0.004	
304L-Re	3016	0.005	
304L-Re	4000	0.005	
304L-Mo/50 Re	840	0.002	No preferential diffusion of any 304L SS component.
304L-Mo/50 Re	1576	0.003	
304L-Mo/50 Re	2184	0.004	
304L-Mo/50 Re	3744	0.005	
304L-W/25 Re	840	0.0005	No preferential diffusion of any 304L SS component.
304L-W/25 Re	1576	0.0008	
304L-W/25 Re	3024	0.001	
304L-W/25 Re	3744	0.0015	
304L-Ta	886	0.0015	Preferential diffusion of nickel and possibly iron.
304L-Ta	1512	0.003	
304L-Ta	3576	0.004	
304L-Ir	816	0.006	Iridium reacted continually. Diff. zone appeared structurally sound.
304L-Pt	1512	0.004	Platinum reacted destructively with outer capsule and with fuel form.

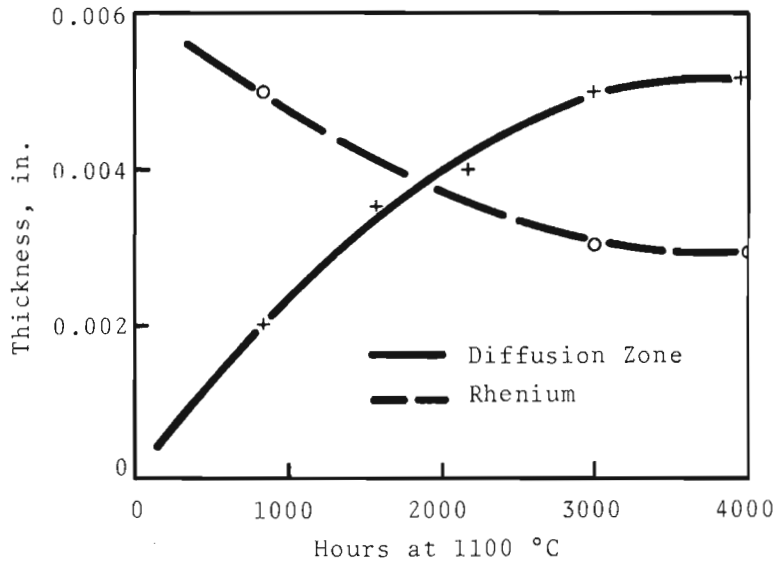


FIGURE 8. 304L SS-Rhenium Reactions

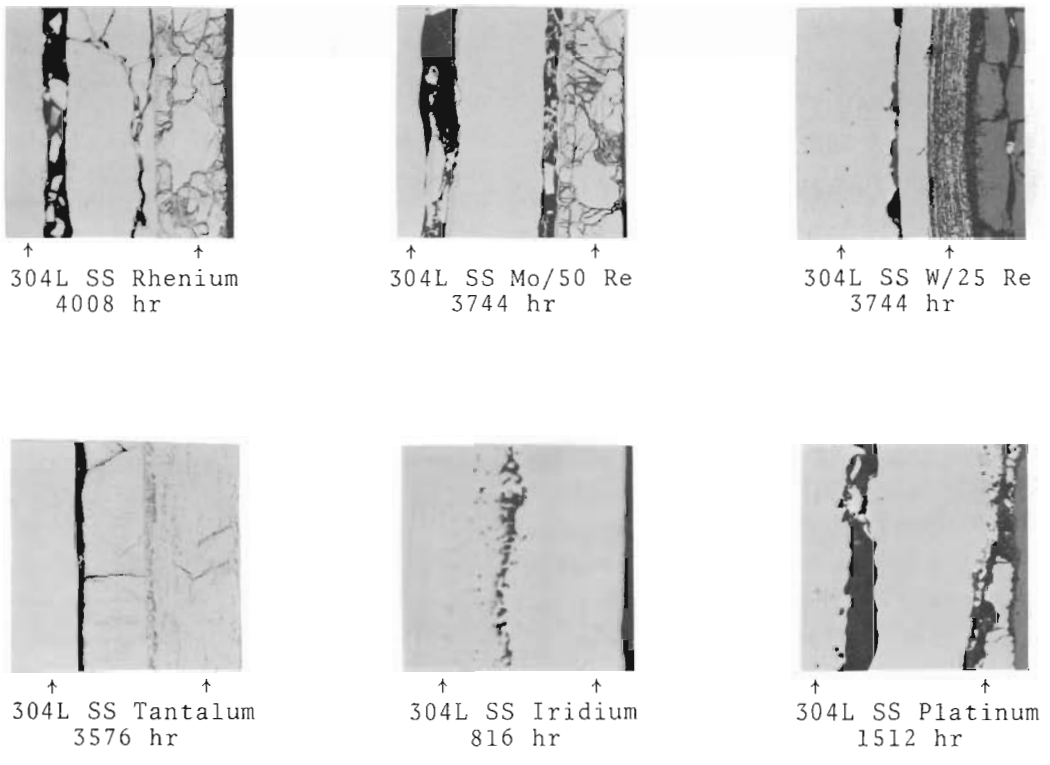


FIGURE 9. Photomicrographs of Metal-Metal Couples Heated at 1100 °C

on the physical properties of the metal and alloy.

Typical metal distributions across the 304L-rhenium couple are illustrated in Figure 10. Distributions across the 304L SS-molybdenum/50 rhenium and 304L-tungsten/25 rhenium couples had the same general features. Metal distributions across the 304L SS-tantalum couple are illustrated in Figure 11. These distributions differed markedly with those for the Hastelloy X or C-tantalum couples, with the only similarity being the nickel and iron peaks at the tantalum-rich side of the diffusion zone. Metal distributions across the 304L SS-iridium couple (Figure 12) help one to understand why the appearance of the couple, as judged from the photomicrograph in Figure 9, originally suggested that only slight reaction had occurred.

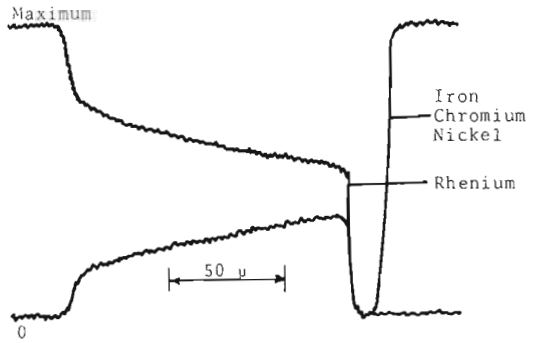


FIGURE 10. Metal Distributions for 304L SS-Rhenium Couple (3016 hr at 1100 °C)

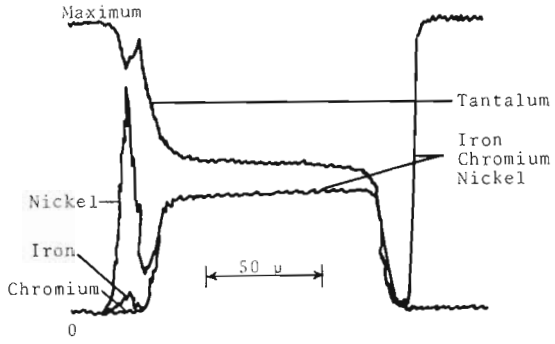


FIGURE 11. Metal Distributions for 304L SS-Tantalum Couple (3576 hr at 1100 °C)

VOLATILITY OF 304L STAINLESS STEEL

The effect of 304L SS volatility on reactions with rhenium, molybdenum/50 rhenium, and tantalum is summarized in Table IV.

Photomicrographs and metal distributions through the foils resulting from heating at 1100 °C are shown in Figure 13. The foils were loosely sealed in 304L SS capsules and had minimal physical contact with the stainless; after the tests they appeared as fully reacted as if they had been in direct contact with the capsules. The foils were much more brittle, however, than when the same metals were used as capsule liners.

The electron microprobe traces gave conclusive demonstration of the major role of volatility of 304L SS components (iron, nickel, chromium) in these metal-metal reactions. Volatility

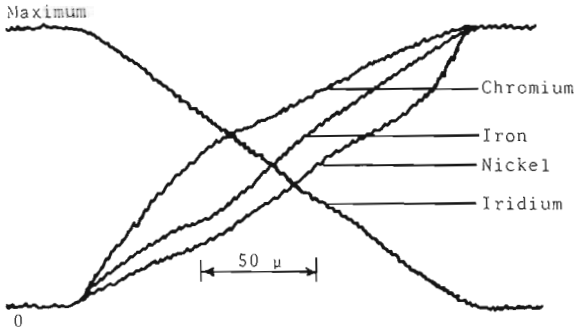


FIGURE 12. Metal Distribution for 304L SS-Iridium Couple (816 hr at 1100 °C)

TABLE IV. Effect of 304L SS Volatility on Metal Foils

Metal Foil	Hours at 1100 °C	Approximate Diff. Zone Thickness, in.	Foil Left Unreacted, in.	Remarks
Rhenium	1680	0.0049	0.0014	X-ray fluorescence shows gross rhenium, iron, chromium at surface. Nickel ∿ 1/10 iron or chromium.
Mo/50 Re	1680	0.0025	0.0021	
Tantalum	1680	0.0007	0.0227	

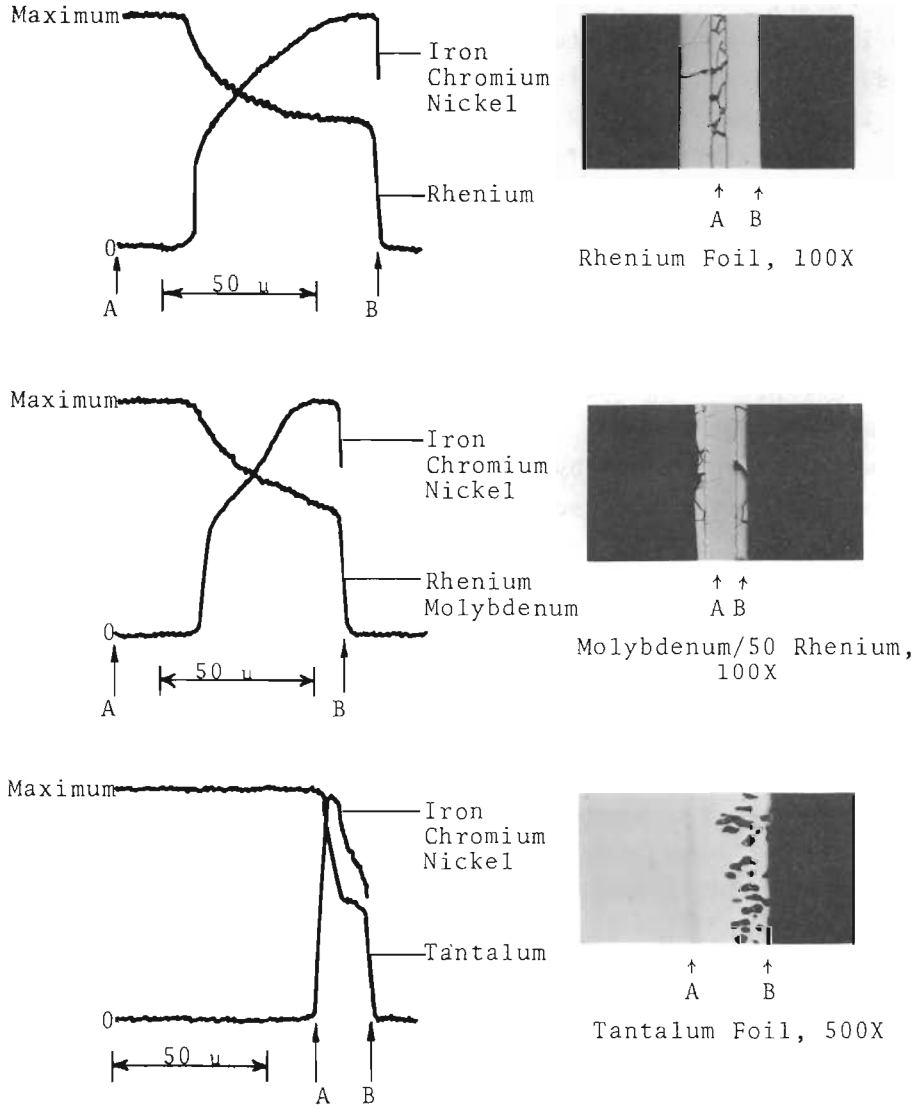


FIGURE 13. Photomicrographs and Metal Distributions in Foils Heated 1680 hr in 304L Capsules at 1100 °C

also explains why, although there was a net diffusion of both 304L SS and the capsule liners, 304L SS was the predominantly mobile force. In these cases, 304L SS components were observed to have by-passed a thin layer of the capsule's contents and diffused into the liner, while the reverse case generally was not observed.

DISCUSSION

The metal-metal couples of this study were prepared by using pneumatic impaction to assure intimate contact between the test metals. In some cases this was detrimental to liners and foils. Rhenium, for example, was adversely affected by the impaction, and less than theoretically dense sites present after preparation of the rhenium foils developed into holes during the impaction. Where only a 0.003 in. rhenium-liner was present in 304L SS capsules heated at 1100 °C for about 3000 to 4000 hr, thorough penetration of the liner by 304L SS components occurred at these "hole" sites. The effect of the impaction on an iridium-lined capsule was even more pronounced. Reactions between slip-fit metallic layers (measured in later experiments) were less extensive than reactions between pneumatically impacted layers.

The slightly different behaviors of Hastelloy X, Hastelloy C, and 304L SS in reactions with potential capsule liners suggest that minor alloy constituents play important roles in limiting the net diffusion of the couples. For example, tungsten is nominally 0.6% and 4%, respectively, of Hastelloy X and Hastelloy C, while the differences between other elemental concentrations are far less. It was noted previously that Hastelloy C exhibited advantages (less reaction with liner metal) over Hastelloy X, which might be attributable, in part, to the different tungsten concentrations. No other correlations with alloy constituent concentrations were noted.

A more pronounced effect of tungsten as a diffusion impeder can be seen from comparison of the alloy-rhenium and alloy-tungsten/25 rhenium couples after similar reaction times. In all cases tungsten/25 rhenium was less reactive than rhenium with the encapsulating alloy. The results suggest that tungsten, or some other as yet unidentified metal, might be advantageously incorporated into a diffusion barrier for the metal-lined fuel capsules.

Metal-metal couples with Hastelloy X, Hastelloy C, or 304L SS all developed void spaces between the diffusion zone and the test alloy, probably during the cooling period after the couples were removed from the furnace. Presently, it is not known whether these voids develop at a relatively high (near 1100 °C) or low temperature, but the accelerated reactions observed after temperature cycling tests suggest that a partial separation may occur at or above 700 °C. The presence of voids would allow surface diffusion to occur, which, together with the effects of volatility and intergranular diffusion, would accelerate the reactions. The effect would be especially noticeable if void formation proceeded directly along the grain boundaries and into the containing alloy.

SUGGESTED FUTURE STUDIES

Hastelloy X and 304L SS reacted similarly with various potential capsule liners. Because of the apparent development of a limiting diffusion

zone thickness with the 304L SS-rhenium couples, the same possibility is suggested for Hastelloy X. Additional long-term tests will be required to verify the 304L SS-rhenium reactions, and to make similar determinations for Hastelloy X and other alloys with rhenium and potential liner metals. Attempts should also be made to determine whether a limiting diffusion zone thickness will be observed following long-term temperature cycling tests.

The tendency of nickel and iron to concentrate when reacted with tantalum suggests that other metals may also undergo similar reactions. Haynes 25 should be tested with tantalum to check this possibility, and tested with other metals to obtain data pertinent to cobalt-base alloys. Other potential encapsulating materials to be tested should include TZM, tantalum/10 tungsten, etc., along with those metals and alloys for which data are presented in this report.

Early efforts should be made to develop and test a diffusion barrier to reduce or eliminate the metal-metal reactions occurring in multilayered capsules. Techniques to be studied might include electroplating, electropolishing, vapor deposition, flame spraying, and the use of ceramic liners. The effects of metal-metal reactions and long-term static and cycling testing on the physical properties of alloys and liner metals should be determined. Higher temperature studies would also provide valuable information.

ACKNOWLEDGEMENTS

The metallographic and electron microprobe analyses were conducted by the Metallography Laboratory, and pneumatic impactions were performed by Materials Process Development Unit. J. D. Cudmore and C. A. Fulcher prepared many of the compatibility couples and test capsules.

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