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ORNL 1774
Metallurgy and Ceramics

DIFFUSION CHARACTERISTICS OF THORIUM AND ALUMINUM

J. A. Milko

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DIFFUSION CHARACTERISTICS OF THORIUM AND ALUMINUM

Work Carried Out by: J. A. Milko

Report Written by: J. A. Milko

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TABLE OF CONTENTS

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[redacted]

[redacted]

LIST OF TABLES

[redacted]

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LIST OF FIGURES

TITLE

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ABSTRACT

Diffusion Characteristics were investigated between thorium and aluminum. The objective of the investigation was to develop information which might serve as a guide in the construction of assemblies for a converter type of reactor utilizing aluminum-clad thorium plates. Extent of the diffusion was evaluated by a measurement of the thickness of the resulting diffusion layer formed between these two metals, in intimate contact, in vacuum.

An appreciable amount of diffusion was observed between thorium and aluminum, particularly in the temperature range of 500 to 600°C. Barriers of aluminum-silicon alloys were not effective in minimizing the diffusion. Alloying of the thorium with beryllium, zirconium, chromium, cerium, vanadium, molybdenum, niobium and tin was not beneficial in decreasing the extent of the diffusion. Alloying of the aluminum with beryllium, chromium, cerium, magnesium plus chromium (52 S) was likewise not effective in reducing the extent of diffusion.

Barriers of magnesium and Nickel, inserted between the thorium and aluminum seemed to have increased the extent of the diffusion. Barriers of zirconium and titanium foil appear to decrease the extent of diffusion at temperatures up to 500°C. At 600°C, the extent of diffusion between zirconium and aluminum is appreciable, while that of titanium and aluminum is somewhat less.

This investigation disclosed that bonding of zirconium and titanium to thorium first occurs at 650°C. From 650°C to 850°C the extent of diffusion between thorium and zirconium or titanium is small.

INTRODUCTION

In the construction of a converter type of reactor, aluminum-clad thorium assemblies were first proposed mostly for reasons of economy. It has been known for some time, that aluminum can be bonded to thorium by the conventional roll cladding techniques. However, only speculation existed concerning the stability of the bond at the brazing temperature of 500 to 600°C, or at the operating temperature (about 225°C) of the fabricated assemblies for extended periods of time.

After careful consideration and review of the requirements of construction and operation of the converter reactor, it was surmised that certain factors will affect the stability of the bond. These are: (1) extent of diffusion of aluminum into thorium during brazing of the assemblies and during the operation, (2) inherent brittleness of the formed diffusion layer, (3) relative expansion characteristics of the

[redacted]

two metals and the formed diffusion layer, (4) resistance to chemical attack of the formed diffusion layer by the ambient water.

Of these factors, probably diffusion and any inherent brittleness of the bond will affect the stability and performance of the assemblies to a marked degree. For that reason it was deemed necessary to investigate the behavior of these two metals in a diffusion couple. The experimental results thus obtained would indicate the feasibility of construction and operation of the assemblies.

The diffusion characteristics between aluminum and thorium were evaluated by exposing the properly prepared contact surfaces at a definite temperature and for predetermined times in a relatively high vacuum. The effect of barriers to the diffusion between these two metals was investigated by placing a thin sheet of barrier material between the contact surfaces. Inherent brittleness of the diffused layers was investigated by means of Knoop hardness measurements across their thickness.

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EXPERIMENTAL WORK

Experimental Procedure for the Investigation of the Diffusion Characteristics of Aluminum into Thorium and Certain Barrier Materials

For the present investigation of the bond and extent of diffusion between aluminum and thorium, the same method was used as for the aluminum and uranium diffusion studies reported earlier.[1] This method consists of "sandwiching" the surface of the cleaned thorium specimen (see Appendix D) of approximately 1/8 in. thickness, 1/2 in. width, and 1 in. length, between two surfaces of cleaned aluminum of similar dimensions. In the present work, the thickness of the aluminum specimens was usually 0.040 in. Such "sandwiches" were then placed into the clamp shown in Fig. 1 (Appendix B), and compressed within the jig to a 7,500 lb. load. They were held at about this load by tightening down of the screw at the top of the clamp. The clamp was then placed into a pyrex or fused silica tube. The large end was next sealed off, and the capillary end of the tube was attached to a vacuum system. Throughout the pump-down period, gentle heat was applied to the tube to facilitate the removal of any adsorbed moisture or gases. When a pressure of less than one micron was obtained,[2] the capillary was sealed off.

The sealed assembly was then taken and placed into a suitable furnace and heated at the desired temperature for a specified period of time. It is appropriate to state at this time, that the "sandwiches" contained in the pyrex tubes withstood prolonged heating up to 550°C, above this temperature fused silica tubes were of distinct advantage. After heating, the assemblies were air cooled in most cases.

When the assemblies cooled sufficiently to permit handling, the "sandwiches" were removed from the clamp, mounted in low temperature plastic, ground, polished, and examined. The measurements of the thickness of the diffused layer were made at high magnification and for that reason any errors were minimized. Furthermore, the reported values are an average of four measurements.

In the attempts to evaluate the effect of barriers, two different methods of approach were used. One of these involved the placing of the

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(1) Terminal Report on ORNL Slug Problem, Causes and Prevention, R. O. Williams, July, 1950.

(2) Measured with a General Electric vacuum gage.

[redacted]

barrier material between the aluminum and thorium, usually in the form of a thin sheet (about 0.010 in. thickness). The other involved a preparation of an alloy with one or the other metals of the diffusion couple, which was then placed into the "sandwich".

Hardness measurements were made across the diffused layer at definite intervals of distance. In most cases at least five determinations were made, and in a few, as many as twenty impressions were made to establish a representative hardness value of a particular location of the diffused layer. A standard load of 100 grams was used throughout with either a 10.25 or 4 mm objective. The values are reported as Knoop hardness numbers.

Effect of Temperature on the Diffusion Layer Thickness of Four Diffusion Couples

In Fig. 2 (Appendix B), and Table 1 (Appendix A), data are presented which show the increase in thickness of the diffusion layer with an increase in temperature. It is evident that at 350°C the diffusion layer thickness is only about 0.003 mm, whereas, at 600°C this thickness is appreciable.

It may also be surmised from the plot of Fig. 2, that in the temperature range of interest, 500-600°C, (probable brazing temperature of the clad assembly plates) the desired effect of the diffusion barriers was not obtained. Thus, the 1.3% and 4.0% silicon-aluminum alloy barriers did not inhibit the growth of the diffusion layer, but actuallly seemed to have promoted it. Although the barrier of 0.65% silicon-aluminum alloy appeared to have decreased the diffusion layer thickness, the decrease was not substantial.

Hardness Survey of the Couples

A Knoop hardness survey was made across the diffusion couples. The results of such a survey are presented in Table 2 (Appendix A) for three positions of each couple. The reported values indicate the abrupt change in hardness from the relatively soft aluminum or thorium to that of the diffusion layer at any particular temperature. It is also apparent from the data, that the hardness of the diffusion layer increases with increasing diffusion temperature. This may not be an entirely correct observation, because it was not always possible to make a satisfactory indentation in the thinner layers formed at the lower temperatures. It is probable that this apparent hardness increase is associated with changes in composition of the diffusion layer.

Microstructure of the Diffusion Layer

Characteristic structures are presented in the views of Figs. 3 and 4, (Appendix B) showing the extent of diffusion and the brittle nature of the four diffusion couples discussed in the foregoing text. Similar structures were observed in the thorium-aluminum couple, and in the thorium -0.65% silicon-aluminum alloy-aluminum couples.

[redacted]

The extreme brittleness of the couples is illustrated by the presence of the thin fracture lines of Fig. 3, and of the large rupture (dark, wide line) between the thorium and the resultant diffusion layer. The complex microstructure of Fig. 4 illustrates the difficulty of obtaining duplicate Knoop hardness values across the diffusion layer.

Variation of Maximum Diffusion Layer Thickness with Time at a Temperature of 350°C

It was brought out in the previous text that severe diffusion occurred at the high temperature of 500-600°C between thorium and aluminum. For that reason, brazing at this temperature was to be avoided. On the other hand, a realatively small amount of diffusion occurred at the 300-400°C temperature range in a four-hour period. It was desirable to determine the rate of diffusion at these temperatures, i.e., 300-400°C, since the contemplated operating temperature in the reactor was in this range.

To provide an answer and to obtain some quantitative data, diffusion couples were prepared and exposed for comparatively long periods of time at 350°C. Such data are presented in Table 3 (Appendix A), and in the plot of Fig. 5 (Appendix B). (Incomplete data are also given for three additional couples because, at the time, elements such as beryllium and zirconium were thought to be probably effective in minimizing diffusion.)

From Table 3, and especially from Fig. 5, it is apparent that the rate of growth of the diffusion layer is very rapid for the first 20 hours and levels off after this period to a very low rate.

Comparing the thickness, after 64 hours at 350°C, to that formed after 4 hours at 500°C, the former is about half of that of the latter. This indicates that perhaps the diffusion layer thickness, at prolonged exposure at low temperature, would not equal that formed at the high temperature. The inference can be made that, were it possible to fabricate the aluminum clad thorium assemblies at low temperature, they would probably perform satisfactorily at the low temperature with duration of time. Further experimental work will be needed to establish this conclusively.

Effect of Alloying Additions in Thorium on the Diffusion Characteristics of the Thorium-Aluminum Couple

Briefly, it may be stated that silicon in the form of an aluminum-silicon alloy had no beneficial effect in decreasing the diffusion of aluminum into thorium. This is particularly true at the high temperature of 500-600°C. For that reason, it was thought worthwhile to investigate other elements or alloys which could be effective in minimizing diffusion.

Examination of the literature on metallic diffusion did not reveal the effectiveness of one possible method of attack on the problem of inhibiting

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diffusion between thorium and aluminum, i.e., would a solid solution alloy of thorium be superior in this respect? To obtain this information, several thorium base alloys were studied in diffusion couples with aluminum. The thorium base alloys that were investigated, and the resulting diffusion layer thicknesses that were obtained are given in Table 4. Hardness measurements are presented in Table 5. Thicknesses of the straight thorium-aluminum couple are also given for purposes of comparison.

Effect of Cerium. It is evident, that the introduction of about 5.0% cerium into the thorium base, (reported to form a solid solution), had an adverse effect. This amount of cerium appears to promote, rather than inhibit, the diffusion of aluminum. Hardness traverses across the couple indicate an abrupt change in hardness within the diffusion layer. The diffusion layer hardness is equivalent to that of the straight thorium-aluminum couple. The microstructure of the diffusion layer is shown in the photograph of Fig. 6. The brittle nature of the layer is exemplified by the rupture that may be observed between the diffusion layer and the aluminum.

Effect of Beryllium. The addition of about 1.7% of beryllium to the thorium (a very small amount was thought to form an interstitial solid solution) had no beneficial effect in minimizing the diffusion. In general, the effect seemed to be one of increasing the diffusion. The resulting diffusion layer developed a high Knoop hardness, somewhat equivalent to that of the straight thorium-aluminum.

Effect of Zirconium. An addition of about 4.0% zirconium to the thorium (this amount is reported to form a solid solution) produced no desirable effect in minimizing the diffusion. The hardness of the resultant diffusion layer is equivalent to that of the straight thorium-aluminum.

Effect of Chromium, Molybdenum, Vanadium, and Niobium. Alloys containing about 8.0% of each element in the thorium were available. Since these elements form eutectics with the thorium, it was of some interest to determine the effect of the presence of a eutectic on the diffusion characteristics of the aluminum. Furthermore, these elements have practically no solid solubility in aluminum, but tend to form compounds. Such a behavior was suggestive of decreasing the diffusion between aluminum and thorium. However, as is apparent from the values of Table 4, the effect of any one of these elements is not beneficial.

The diffusion layer thickness of the thorium-chromium alloy is about three times that of the straight thorium-aluminum. The hardness of the diffusion layer is high, suggesting brittleness.

The diffusion layer thickness of the thorium-molybdenum, thorium-vanadium, and thorium-niobium appears to be about twice that of the straight thorium-aluminum. The Knoop hardness of the resultant layers is quite high.

The unetched structure of the diffusion layer formed between the thorium-chromium alloy and aluminum is shown in the photograph of Fig. 7. Although

[redacted]

this view does not show many of the fine fractures observed in the diffusion layer, it is quite brittle. The other diffusion layers are quite similar.

Effect of Tin. An alloy of thorium with 2.0% tin was available. This was used for preparation of a diffusion couple, chiefly because of the consideration that tin and aluminum were stated to be immiscible in the liquid and solid state.

From Table 4, it is evident that the tin had no beneficial effect. The Knoop hardness of the diffusion layer is rather high, as compared to the straight thorium-aluminum.

Effect of Carbon. Carbon was considered as an addition to the thorium with a view of decreasing the diffusion of aluminum, mainly because small amounts of carbon may form interstitial solid solution and above this amount the carbon tends to form carbides of thorium. It was thought possible that both of the phases might minimize diffusion of aluminum into thorium. Alloys were prepared, ranging in carbon content from 0.05 to 0.18% (intended), and diffusion couples were made from such alloys.

Although no diffusion data are presented, the results were inconclusive. From the erratic data obtained, it is not possible to deduce whether carbon is beneficial or detrimental.

Effect of Alloying Additions to the Aluminum on the Diffusion Characteristics of the Thorium-Aluminum Couple.

It is obvious from the previous discussion, that alloying of the thorium had no beneficial effect of minimizing the diffusion of aluminum into the thorium. It was thought, that perhaps if the aluminum were alloyed, the desired effect might be obtained. In Table 6, data are presented for six diffusion couples in which the aluminum was alloyed. Hardness values of these couples are presented in Table 7. The values obtained on the straight thorium-aluminum couple are also presented for comparison purposes.

Effect of Beryllium. One of the first alloying additions attempted with the aluminum, was beryllium. This element was stated to minimize the thickness of the $FeAL_3$ compound layer formed in the dipping of iron into molten aluminum. On this basis it was investigated in these studies.

The effects of beryllium additions to aluminum on the diffusion layer thickness were rather erratic. Its effect on the hardness of the layer is somewhat questionable.

Effect of Chromium. The effect of chromium in the form of aluminum-1.0% chromium alloy, and also in the 52 S type aluminum (0.25% Cr, 2.5% Mg) was investigated. Chromium, when present in either alloy, seems to have an undesirable effect. Thickness values, approximately twice those of the straight thorium-aluminum couples, were obtained. The hardness values of the resultant

[redacted]

diffusion layers are equivalent to those found for the straight thorium-aluminum diffusion layer.

The structures of the diffusion layers formed between the interaction of the aluminum-chromium alloys and thorium are shown in Figs. 8, 9, and 10. The complexity of the structures of the 52 S alloy diffusion should be noted.

Effect of Cerium. Cerium was known to form a eutectic with aluminum at about 11 weight percent. It was desirable to note the effect of this eutectic on the diffusion into thorium. Comparable diffusion layer thicknesses were obtained as those for the straight thorium-aluminum. Likewise, similar hardness values were obtained for the diffusion layer.

Alloying of the thorium with 5.0% cerium resulted in diffusion thicknesses somewhat greater than those in which the aluminum was alloyed with 11.0% cerium. This may or may not be significant. In the present consideration, it is of no significance.

Effect of Sintered Aluminum Powder. A product, resulting from an intimate ball milling of angular, oxidized aluminum powder, followed by sintering, was thought to be effective in minimizing diffusion. One diffusion couple was prepared from this material in contact with thorium. After four hours at 500°C, the amount of diffusion was considerable; however, the diffusion layer thickness was rather erratic, being considerably greater in certain locations than in others, as shown in Fig. 11. There appeared to be no satisfactory bond between the diffusion layer and the sintered aluminum powder base. The hardness of the diffusion layer was rather high.

Effect of Magnesium and Nickel on the Diffusion Characteristics of the Thorium-Aluminum Couple

In a concurrent separate investigation of diffusion, (see Appendix C) it was observed that uranium-magnesium couples showed essentially no diffusion at temperatures as high as 600°C. It was thought that magnesium might be as inert to thorium. For that reason, magnesium-thorium and magnesium-thorium-aluminum diffusion couples were tested. Nickel was investigated mostly to remove all doubt of it's ineffectiveness as a barrier. The data obtained on these three couples are presented in Table 8. Hardness values are given in Table 9. The values of the thorium-aluminum couple are listed for comparison.

Magnesium diffuses to about the same extent as does aluminum at 400°C. At 500 and 600°C the diffusion layer thickness of the thorium-magnesium couple is about three times that formed between thorium-aluminum. There appears to be a break in the bond between the magnesium and the diffusion layer as shown in Fig. 12. The resultant diffusion product appears to be very brittle.

In the couple prepared from aluminum and thorium, where the magnesium was used as a barrier, appreciable diffusion of the magnesium occurred into the thorium. A very complex brittle structure was formed, as may be observed from the photograph of Fig. 13.

A diffusion couple was prepared from aluminum and thorium in which nickel was used as a barrier. After such a couple was heated for four hours at 600°C, a diffusion product formed which had appreciable thickness and a very complex structure as seen in Fig. 14.

Diffusion Characteristics of Zirconium and Titanium into Thorium

Several considerations led to an investigation of the diffusion characteristics of zirconium and titanium in contact with thorium. One of these was to determine the temperature required to initiate bonding, and to what extent diffusion would occur. Should the diffusion be limited, then perhaps these two metals might be utilized as barriers in the thorium-aluminum couple. Later, as a result of the data obtained, it was necessary to prepare diffusion couples of aluminum with titanium and zirconium and evaluate the extent of the diffusion.

The first couple that was studied was the thorium-zirconium. From the data of Table 10, it is apparent that no diffusion or bonding takes place between thorium and zirconium until a temperature of 650-700°C is reached. The extent of diffusion observed in the temperature range of 700-850°C is relatively small. This appeared to be an indication that perhaps zirconium could be used as a barrier against the diffusion of aluminum into thorium.

Although tests were not made on the thorium-titanium couple in the temperature range of 200-600°C, it is expected that no diffusion or bonding occurred, as in the thorium-zirconium couple. Certainly in the temperature range of 650-850°C the extent of diffusion between thorium and titanium was about the same as in thorium-zirconium.

The extent of the diffusion of zirconium and titanium into thorium is illustrated in Figs. 15 and 16, respectively. The diffusion layer thickness is very small, and several breaks in the bond were observed in the layers of the samples that were examined.

Diffusion Characteristics of Zirconium and Titanium into Aluminum

Since the diffusion of zirconium and titanium into thorium was of a limited extent, it was reasoned that perhaps the thorium could be clad first at the higher temperature with either the zirconium or titanium, and then clad with aluminum at a lower temperature. Such techniques required that data be obtained on the extent of diffusion of zirconium and titanium into aluminum. Tests were made on diffusion couples of zirconium-aluminum and titanium-aluminum. The extent of diffusion of zirconium and titanium in contact with aluminum is presented in Table 11 in the form of thickness measurements of the resultant diffusion layer. Hardness values are given in Table 12.

[redacted]

From Table 11, it is apparent that no diffusion nor bonding occurs in the temperature range 200 to 375°C between zirconium and aluminum. Although no tests were conducted on the titanium-aluminum couple, no bonding or diffusion is expected in this temperature range. At 400°C, satisfactory bonding occurs in both couples without the formation of a measurable thickness of the diffusion layer. At 500 and 600°C, appreciable diffusion layer thickness is formed in the zirconium-aluminum couple, and slightly less in the titanium-aluminum couple.

The very thin diffusion layer formed between titanium and aluminum at 500°C is illustrated in Fig. 17. The measurable thickness of the diffusion layer, after four hours at 600°C, and its inherent brittleness is shown in Fig. 18. Figs. 17 and 18 illustrate the apparently critical dependence of the diffusion layer thickness on temperature.

In summary, it may be stated that although the diffusion of either zirconium or titanium into thorium is relatively slow in the temperature range of 500 to 600°C, and the extent of their diffusion is limited, they cannot be used as barriers to inhibit the diffusion of aluminum into thorium. The diffusion of aluminum into zirconium and into titanium is appreciable at 600°C. The diffusion of aluminum into titanium at 500°C appears to be limited. On the basis of these data, there is some possibility that titanium might serve as a diffusion barrier between aluminum and thorium at 500°C. However, brazing of aluminum-clad thorium plates into reactor components at this temperature would be exceedingly difficult with conventional aluminum brazing alloys.

Acknowledgement

Throughout this investigation, the continued interest, guidance and encouragement of Mr. E. J. Boyle is gratefully acknowledged. The aid received from certain members of the fabrication and metallography group, in the preparation of alloys and samples is likewise acknowledged. Particular acknowledgment is given to R. T. Clem for his careful preparation and assembly of the diffusion samples, measurements of thickness and determination of hardness of the diffusion layers.

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Table I. **Measured Thickness, Millimeters, of the Diffusion Layer After Four Hours at the Indicated Temperatures of Four Diffusion Couples**

Diffusion Couple	200	300	350		375		400		450		475		500		600	
			Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Th-Al	(a)	(a)	0.003(1)	0.0009(1)	(b)	(b)	0.012(1)	0.003(1)	0.015(1)	0.001(1)	0.025(1)	0.006(1)	0.023(1)	0.005(1)	0.051(1)	0.008(1)
			0.004(1)	0.001(1)	0.004(1)	0.001(1)			0.010(1)	0.002(1)						
Th-.65% Si-Al Alloy-Al	(a)	(a)	0.002(1)	0.0009(1)	0.003(1)	0.001(1)	0.014(1)	0.006(1)	0.012(1)	0.003(1)	0.013(1)	0.003(1)	0.019(1)	0.004(1)	0.042(1)	0.006(1)
			0.004(2)		0.007(1)	0.001(1)										
Th-1.3% Si-Al Alloy-Al	-	-	(b)	(b)	0.006(1)	0.001(1)	-	-	0.008(1)	0.002(1)	0.021(1)	0.006(1)	0.033(1)	0.006(1)	0.095(1)	0.032(1)
Th-4% Si-Al Alloy-Al	[redacted]	-	0.003(3)	(b)	0.004(3)	(b)	-	-	0.008(1)	0.002(1)	0.025(1)	0.003(1)	0.034(1)	0.003(1)	0.135(1)	[redacted](1)

(a) No apparen[redacted]ffusion layer nor bond.
(b) Apparently satisfactory bond formed without a measurable diffusion layer.

(1) **Average of four thickness measurements.**
(2) **Average of three thickness measurements.**
(3) **A single thickness measurement.**

[redacted]

Table 2. Knoop Hardness Values at the Given Locations in Four Diffusion Couples After Heating for Four Hours at the Indicated Temperatures

		Knoop Hardness Values				
		Temperature, °C				
Diffusion Couple	Position in Couple	400	500		600	
Th-Al	In Aluminum	22	23	21	26	21
Th-Al	In Diffusion Layer	152	226	344(1)	430	472(1)
Th-Al	In Thorium	80	61	67	63	67
Th-0.65% Si	In Aluminum	21	26	17	31	
Al Alloy-Al	In 0.65% Si-Al Alloy	30	36	28	36	
Al Alloy-Al	In Diffusion Layer	142	292	295	437	
Al Alloy-Al	In Thorium	86	80	52	68	
Th-1.3% Si	In Aluminum	-	20		27	
Al Alloy-Al	In 1.3% Si-Al Alloy	-	39		33	
Al Alloy-Al	In Diffusion Layer	-	344		510	
Al Alloy Al	In Thorium	-	88		79	
Th-4% Si	In Aluminum	-	26		29	
Al Alloy-Al	In 4.0% Si-Al Alloy	-	47		34	
Al Alloy-Al	In Diffusion Layer	-	336		487	
Al Alloy-Al	In Thorium	-	83		84	

(1) A recheck.

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Table 3. Measured Thickness, Millimeters, of the Diffusion Layer, After an Exposure at 350°C For the Indicated Time

Time, Hours at 350°C

Diffusion Couple	4		8		16		32		64	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Th-Al	0.003(1)	0.0009(1)	0.006(1)	0.001(1)	0.011(1)	0.003(1)	0.010(1)	0.002(1)	0.010(1)	0.003(1)
	0.004(1)	0.001(1)								
Th-.65% Si-Al Alloy-Al	0.002(1)	0.0009(1)	0.009(1)	0.003(1)	0.014(1)	0.003(1)	0.011(1)	0.003(1)	0.013(1)	0.002(1)
	0.004(2)									
Th-1.3% Si-All[redacted]y-Al	(b)	(b)	0.006(1)	0.001(1)	0.003(3)	-	(a)	(a)	0.003(1)	0.001(1)
Th-4% Si-Al Al[redacted]l	0.003(3)		0.005(1)	0.001(1)	0.016(1)	0.003(1)	0.007(1)	0.001(1)	0.011(1)	0.002(1)
Th-1% Be-Al Alloy-Al	(b)	(b)	-	-	-	-	-	-	0.006(1)	0.001(1)
1.7% Be-Th Alloy-Al	0.004(1)	0.001(1)	-	-	-	-	-	-	0.016(1)	0.005(1)
4% Zr-Th Alloy-Al	0.004(1)	-	-	-	-	-	-	-	0.010(1)	-

(a) No apparent diffusion layer nor bond.
(b) Apparently satisfactory bond formed without a measurable diffusion layer.

(1) Average of four thickness measurements.
(2) Average of three thickness measurements.
(3) A single thickness measurement.

[redacted]

Table 4. Measured Thickness, Millimeters, of the Diffusion Layer of Several Diffusion Couples After Four Hours at the Indicated Temperatures

Temperature, °C

Diffusion Couple	400		500		600	
	Max	Min.	Max.	Min	Max.	Min.
	mm	mm	mm	mm	mm	mm
Th-Al	0.012(1)	0.003(1)	0.023(1)	0.005(1)	0.051(1)	0.008(1)
5% Ce-Th Alloy-Al	-	-	0.035(1) 0.030(1)	0.007(1) 0.006(1)	0.076(1)	0.016(1)
1.7% Be-Th Alloy-Al	0.004(1)	0.001(1)	0.070(1)	0.041(1)	0.05[illegible](1)	0.013(1)
4% Zr-Th Alloy-Al	0.004(1)	-	0.056(1)	0.021(1)	0.04[illegible](1)	0.008(1)
8% Cr-Th Alloy-Al	-	-	0.076(1)	0.006(1)	0.122(1)	0.023(1)
8% Mo-Th Alloy-Al	-	-	0.044(1)	0.006(1)	0.037(1)	0.007(1)
8% V-Th Alloy-Al	-	-	0.040(1)	0.005(1)	0.044(1)	0.005(1)
8% Nb-Th Alloy-Al	-	-	0.035(1)	0.009(1)	0.079(1)	0.006(1)
2% Sn-Th Alloy-Al	-	-	0.036(1)	0.004(1)	0.057(1)	0.008(1)

(1) A recheck.

[redacted]

[redacted]

Table 5. Hardness Values Obtained in the Given Locations on Several Diffusion Couples

Knoop Hardness Values

Diffusion Couple	Position in Couple	Temperature, °C: 400	500		600	
Th-Al	In Aluminum	22	23	21(1)	26	21
Th-Al	In Diffusion Layer	152	226	344(1)	430	472(1)
Th-Al	In Thorium	80	61	67(1)	63	67
5% Ce-Th	In Aluminum	-	18		23	
Alloy-Al	In Diffusion Layer	-	353		410	
Alloy-Al	In 5% Ce-Th Alloy	-	64		64	
1.7% Be-Th	In Aluminum	-	26		21	
Alloy-Al	In Diffusion Layer	-	482		466	
	In 1.7% Be-Th Alloy	-	102		96	
4% Zr-Th	In Aluminum	-	24		23	
Alloy-Al	In Diffusion Layer	-	461		466	
	In Thorium	-	88		89	
8% Cr-Th	In Aluminum	-	20		23	
Alloy-Al	In Diffusion Layer	-	445		489	
	In 8% Cr-Th Alloy		118		104	
8% Mo-Th	In Aluminum	-	20		21	
Alloy-Al	In Diffusion Layer	-	410		406	
	In Thorium	-	90		85	
8% V-Th	In Aluminum	-	23		21	
Alloy-Al	In Diffusion Layer	-	453		431	
	In Thorium	-	93		81	
8% Nb-Th	In Aluminum	-	22		24	
Alloy-Al	In Diffusion Layer	-	319		396	
	In Thorium	-	148		89	
2% Sn-Th	In Aluminum	-	46		63	
Alloy-Al	In Diffusion Layer	-	681		712	
	In Thorium	[redacted]	356		373	

(1) A recheck.

[redacted]

[redacted]

[redacted]

Table 6. Measured Thickness, Millimeters, of the Diffusion Layer, After Four Hours at the Indicated Temperature of Several Couples

Temperature, °C

Diffusion Couple	400		500		600	
	Max	Min	Max	Min	Max	Min
Th-Al	0.012(1)	0.003(1)	0.023(1)	0.005(1)	0.051(1)	0.008(1)
Th-1% Be-Al Alloy-Al	(b)	(b)	0.040(1)	0.014(1)	0.022(1)	0.009(1)
Th-52 S-Al	-	-	0.040(1)	0.009(1)	0.23(1)	0.08(1)
Th-52 S	-	-	0.050(1)	0.02(1)	0.16(1)	0.04(1)
Th-S.A.P.*	-	-	0.034(1) 0.056(1)	- 0.014(1)	- -	- -
Th-1% Cr-Al Alloy	-	-	0.045(1)	0.008(1)	0.086(1)	0.005(1)
Th-11% Ce-Al Alloy	-	-	0.027(1) 0.036(1)	0.004(1) 0.006(1)	0.056(1)	0.008(1)

(b) Apparently good bond without measurable diffusion layer.

* Sintered aluminum powder containing up to 25% aluminum oxide.

(1) Average of four thickness measurements.

[redacted]

[redacted]

[redacted]

Table 7. Hardness Values Obtained in the Given Location of Several Diffusion Couples

Knoop Hardness Values

Diffusion Couple	Position in Couple	Temperature, °C 400	500	600
Th-Al	In Aluminum	22	23, 21	26, 21
Th-Al	In Diffusion Layer	152	226, 344(1)	430, 472(1)
Th-Al	In Thorium	80	61, 67	63, 67(1)
Th-1% Be-Al Al Alloy	In Aluminum	-		
	In 1% Be-Al Alloy	-	26	26
	In Diffusion Layer	-	355	364
	In Thorium	-	68	69
Th-52 S-Al	In Aluminum	-	-	-
	In Al-52 S			86
	In Diffusion Layer			436
	In Thorium			72
Th-S.A.P.	In S.A.P.	-	96	-
	In Diffusion Layer	-	422	-
	In Thorium	-	63	-
Th-1% Cr Al Alloy	In 1% Cr-Al Alloy	-	40	100
	In Diffusion Layer	-	336, 357(1)	449
	In Thorium	-	74	185
Th-11% Ce Al Alloy	In 11% Ce-Al Alloy	-	51	45
	In Diffusion Layer	-	289	471
	In Thorium	-	73	79

(1) A recheck.

[redacted]

[redacted]

Table 8. Measured Thickness, Millimeters, of the Diffusion Layer, After Four Hours at the Indicated Temperature of Three Diffusion Couples

Diffusion Couple	400		500		600	
	Max	Min	Max	Min	Max	Min
Th-Al	0.012(1)	0.003(1)	0.023(1)	0.005(1)	0.051(1)	0.008(1)
Th-Mg	0.012(2)	0.004(2)	0.078(1)	0.040(1)	0.146(1)	0.092(1)
			0.096(1)	0.018(1)		
Th-Mg-Al	0.028(1)	0.006(1)	0.034(1)	0.013(1)	-	-
			0.398(1)	0.090(1)		
Th-Ni-Al	-	-	-	-	0.15(1)	0.04(1)

Temperature, °C

(1) Average of four readings.

(2) Average of two readings.

[redacted]

[redacted]

Table 9. Hardness Values Obtained in the Given Location on Thorium-Magnesium Couples After Four Hours at the Indicated Temperature

Knoop Hardness Values

Diffusion Couple	Position in Couple	Temperature, °C 400	500	600
Th-Al	In Aluminum	22	23, 21(1)	26, 21(1)
Th-Al	In Diffusion Layer	152	226, 344(1)	430, 472(1)
Th-Al	In Thorium	80	61, 67(1)	63, 67(1)
Th-Mg	In Magnesium	29	30, 30(1)	92, 94(1)
[redacted]-Mg	In Diffusion Layer	40	287, 307(1)	25[redacted] 367(1)
[redacted]-Mg	In Thorium	75	86, 89(1)	73[redacted]
[redacted]-Mg-Al	In Aluminum	23	252	-
Th-Mg-Al	In Magnesium	30	348	-
Th-Mg-Al	In Diffusion Layer	186, 232(2)	454	
Th-Mg-Al	In Thorium	76	75	-

(1) A recheck.

(2) Values obtained in bonded portion.

[redacted]

[redacted]

Table 10. Measured Thickness, Millimeters, of the Diffusion Layer After Four Hours at the Indicated Temperatures of Two Diffusion Couples

Temperature, °C

Diffusion Couple	200	300	350	375	400	500	600	650	700	750		800		850	
										Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Th-Zr	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(b)	(b)	0.002(1)	0.001(1)	0.003(2)	0.001(2)	0.002(2)	(b)
								(b)	0.005(1)					0.02(1)	0.001
Th-Ti	-	-	-	-	-	-	-	0.002(3)	0.005(3)	0.002(2)	(b)	0.004(3)	(b)	0.002(3)	0.001(3)
												0.008(4)	0.001(4)	0.003(3)	(b)

(a) No apparent diffusion layer or bond.
(b) Irregular diffusion layer and bond ruptured in spots.
(1) Average of three thickness measurements.
(2) A single thickness measurement.
(3) Average of two thickness measurements.
(4) Average of ten thickness measurements.

[redacted]

[redacted]

Table 11. Measured Thickness, Millimeters, of the Diffusion Layer After Four Hours at the Indicated Temperatures of Two Diffusion Couples

Temperature, °C

Diffusion Couple	200	300	350	375	400		450		500		600	
					Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Zr-Al	(a)	(a)	(a)	(a)	(b)	(b)	0.010 (2)	0.002 (2)	0.039 (1)	0.003 (1)	0.047 (1)	0.004 (1)
					(b)	(b)			0.042 (1)	0.010 (1)	0.058 (1)	0.004 (1)
									0.034 (1)	0.005 (1)	0.062 (1)	0.005 (1)
									0.038 AV	0.006 AV	0.056 AV	0.004 AV
Ti-Al	-	-	-	-	(b)	(b)	-	-	(b)	(b)	0.036 (3)	0.005 (3)
									(b)	(b)	0.028 (3)	0.006 (3)
[redacted]											0.043 (1)	0[redacted]5 (1)
											0.036 AV	0[redacted]9 AV

(a) No apparent diffusion layer nor bond.

(b) Apparently satisfactory bond formed without a measurable diffusion layer.

(1) Average of four thickness measurements.

(2) Average of three thickness measurements.

(3) Average of eight thickness measurements.

[redacted]

Table 12. Hardness Values Obtained in the Given Locations on Aluminum-Zirconium and Aluminum-Titanium Couples After Four Hours at Indicated Temperature

Knoop Hardness Values

Diffusion Couple	Position in Couple	Temperature, °C: 500	Temperature, °C: 600
Zr-Al	In Aluminum	23, 44(1); 24, 24(1)(3)	21, 46(1); 23, 90(1)(3)
Zr-Al	In Diffusion Layer	592, 459(3)	657, 522(3)
Zr-Al	In Zirconium	96, 102(2); 101, 172(2)(3)	113, 166(2); 89, 158(2)(3)
Ti-Al	In Aluminum	23, 36(1)	25, 33(1); 236(1)(3)
Ti-Al	In Diffusion Layer	-	382, 359(3)
Ti-Al	In Titanium	121, 107(2)	126, 123(2); 119(3)

(1) In aluminum adjacent to zirconium or titanium.
(2) In zirconium or titanium adjacent to aluminum.
(3) A recheck on another diffusion couple.

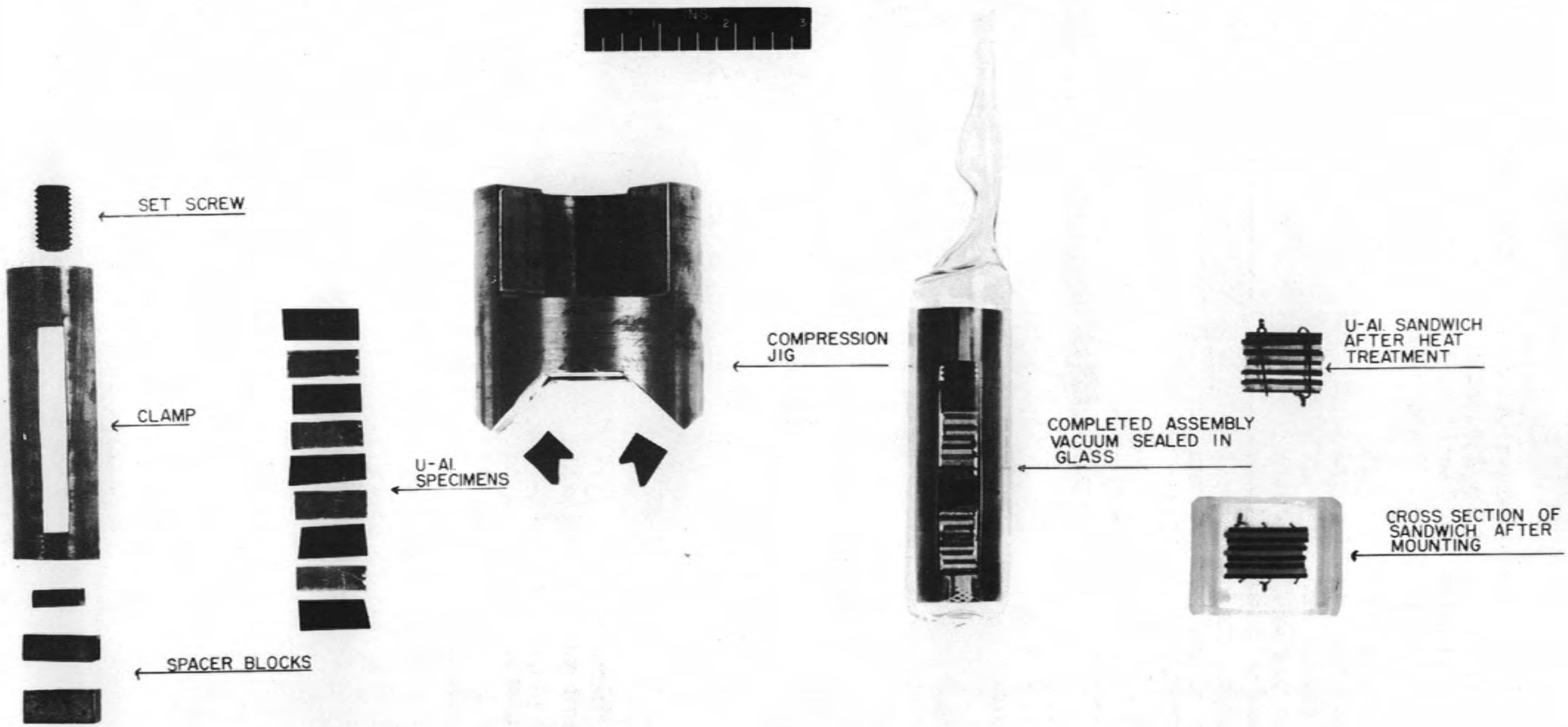


Fig. 1. Components and Assembly Used in the Diffusion Studies. 1X

[redacted]
ORNL—LR—DWG 2631

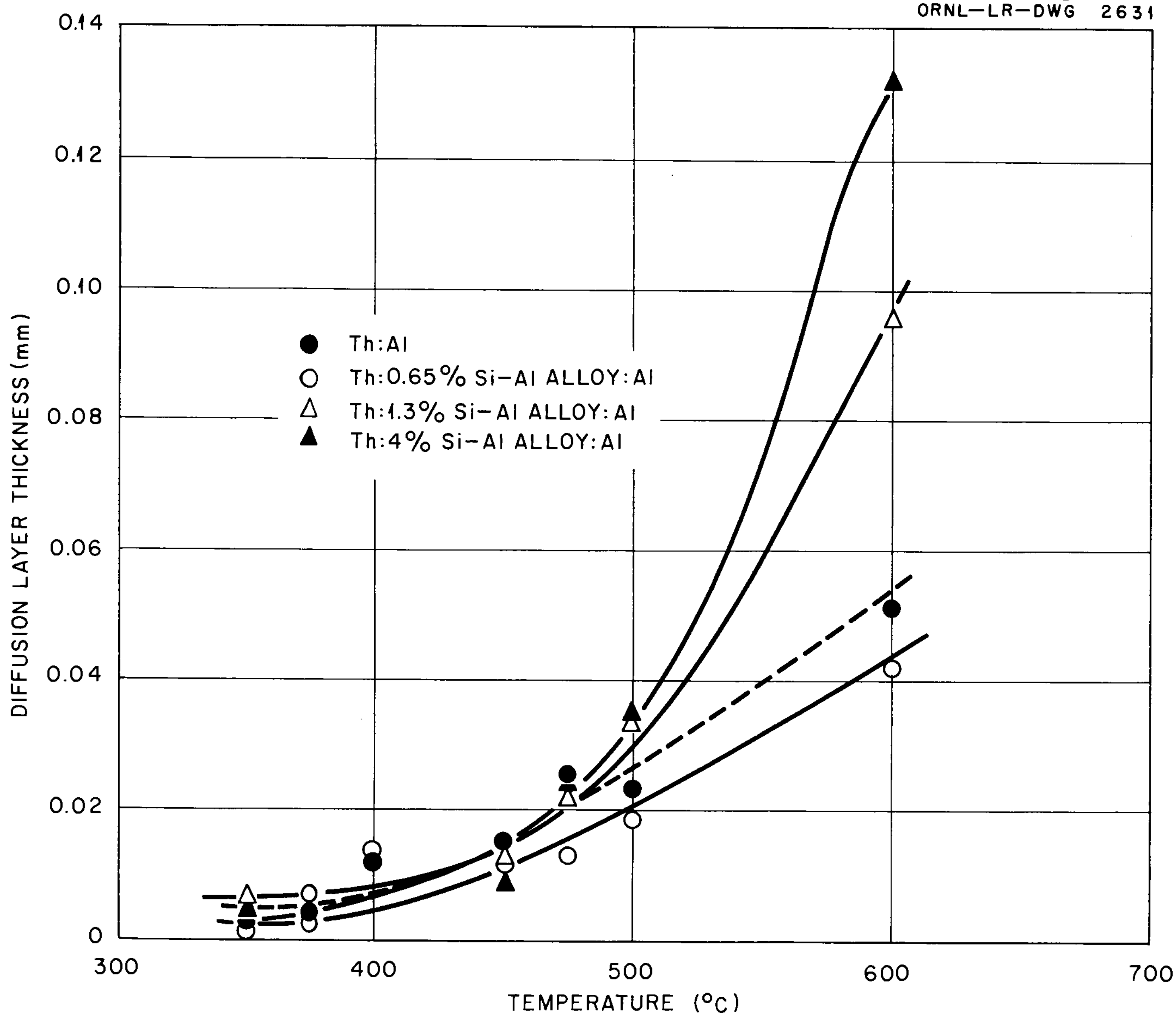
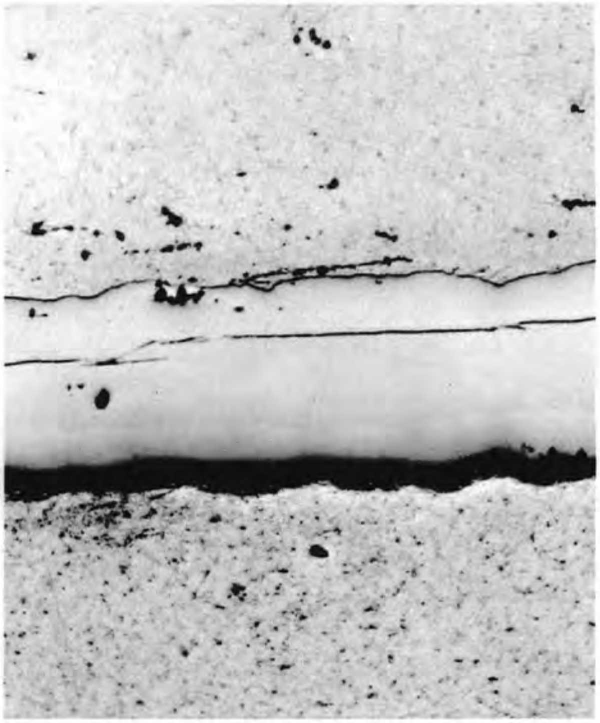


Fig. 2. Variation of Maximum Diffusion Layer Thickness of Four Diffusion Couples With Temperature.

[redacted]

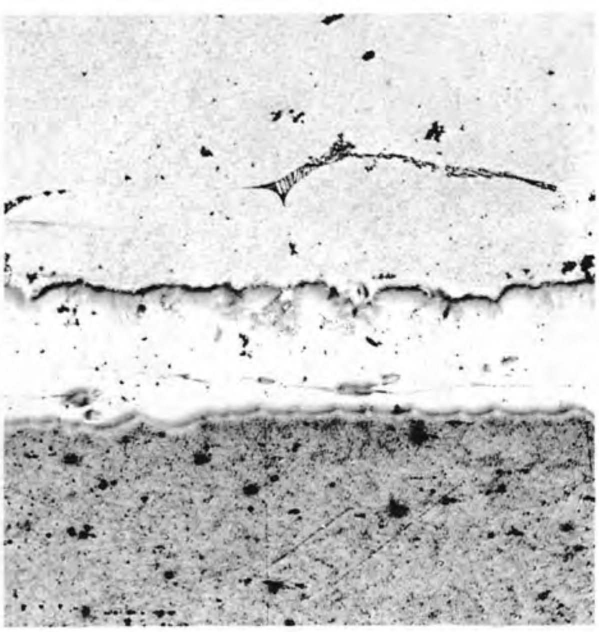


--1.3% Si-Al Y-9850

Fig. 3. Appearance of the Diffusion Layer After Four Hours at 600°C. The original couple consisted of a sheet of 1.3% silicon-aluminum alloy placed between a sheet of thorium (lower part of photograph) and aluminum (upper portion of photograph). Unetched. 250X

--Diffusion Layer

--Thorium



--4% Si-Al Y-9839

Fig. 4. Appearance of the Diffusion Layer After Four Hours at 600°C. The original couple consisted of a sheet of 4% silicon aluminum alloy placed between a sheet of thorium (lower portion) and aluminum (upper portion). Unetched. 100X

--Diffusion Layer

--Thorium

[redacted]

[redacted] [redacted]

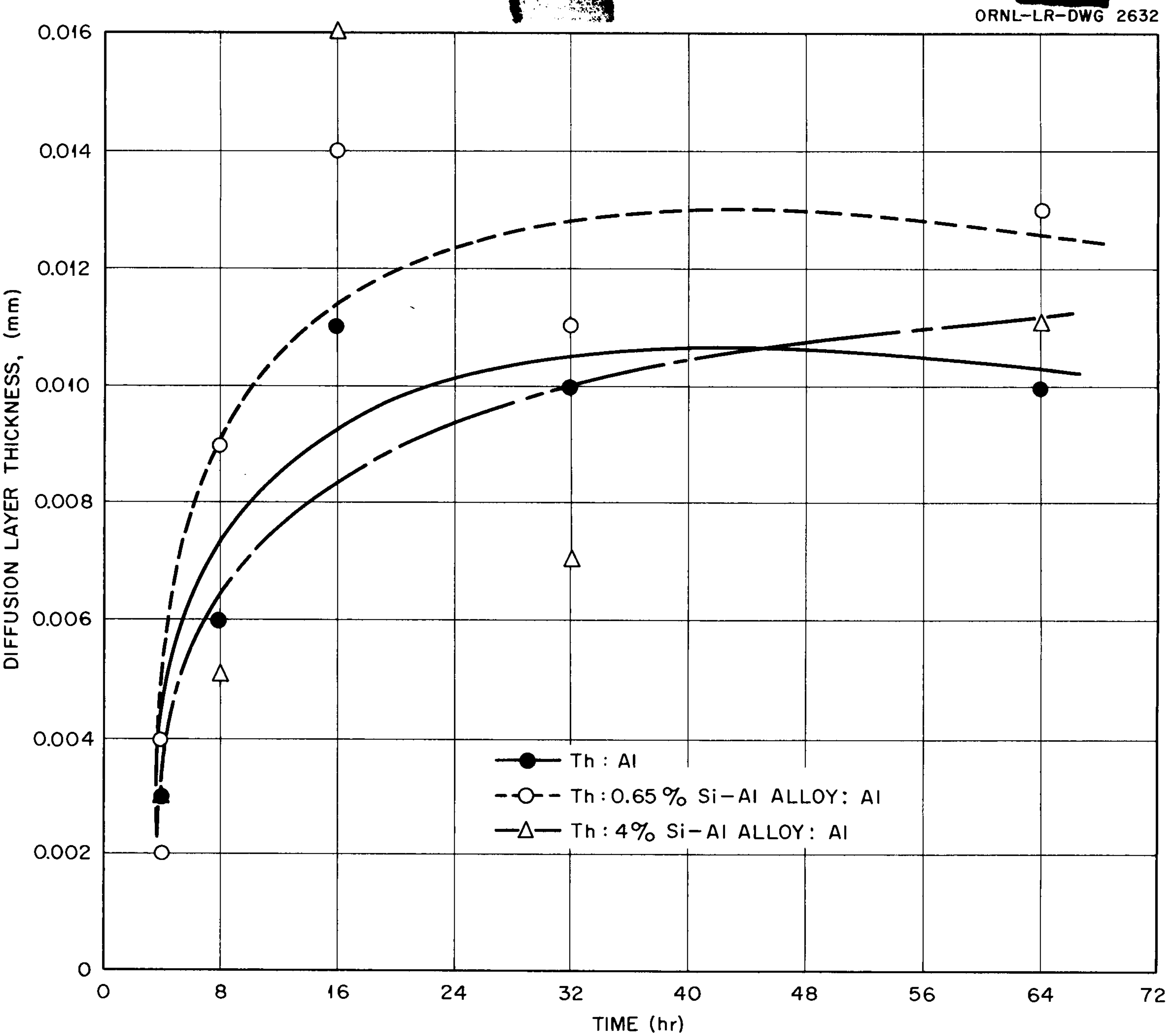
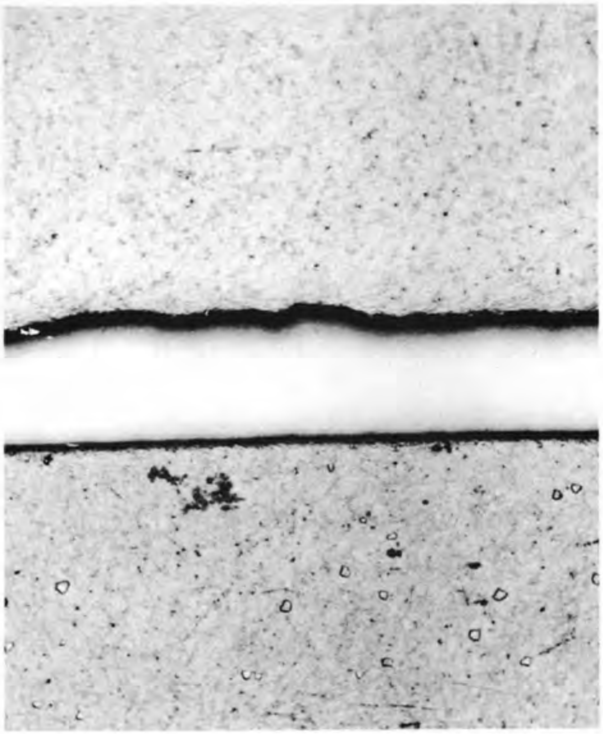


Fig. 5. Variation of Maximum Diffusion Layer Thickness of Three Diffusion Couples With Time, at a Temperature of 350°C.

[redacted]



-Al

-Diffusion Layer

-Ce-Th

Y-9849

Fig. 6. Appearance of the Diffusion Layer of the Thorium -5% Cerium Alloy, Aluminum Diffusion Couple. The original thorium -5% cerium alloy appears in the (lower portion of the photograph). Heated four hours at 600°C.
Unetched. 250X

Y-9842

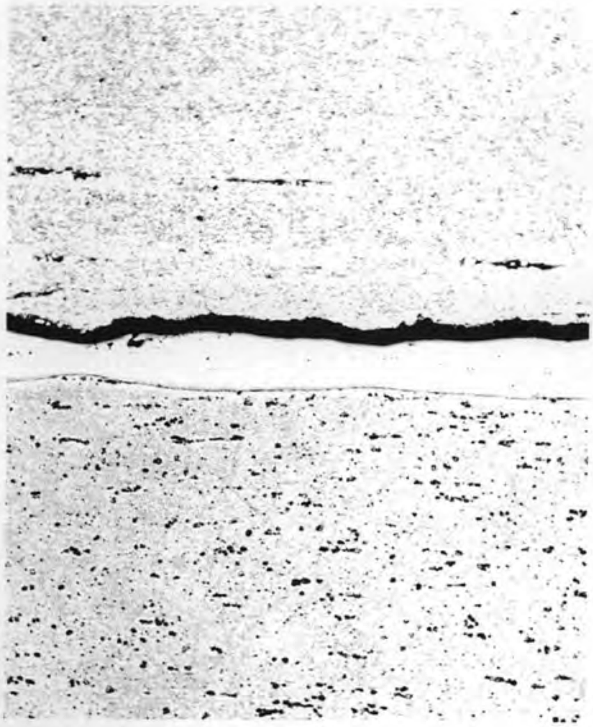
--Al

--Diffusion Layer

--Th-Cr

Fig. 7. Appearance of the Diffusion Layer Formed Between a Thorium 8% Chromium Alloy (lower portion of photograph) and Aluminum After Four at 600°C.
Unetched 100X

[redacted]

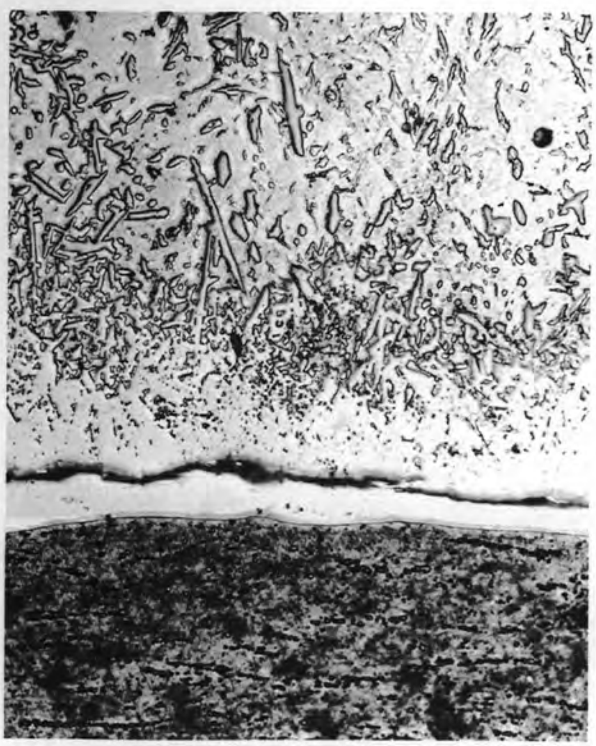


- Al-Cr Y-9851

Fig. 8. Appearance of the Diffusion Layer Formed Between Aluminum-1% Chromium Alloy (upper portion of photograph) and Thorium After Four Hours at 600°C.
Etched with HF 100X

- Diffusion Layer

--Th



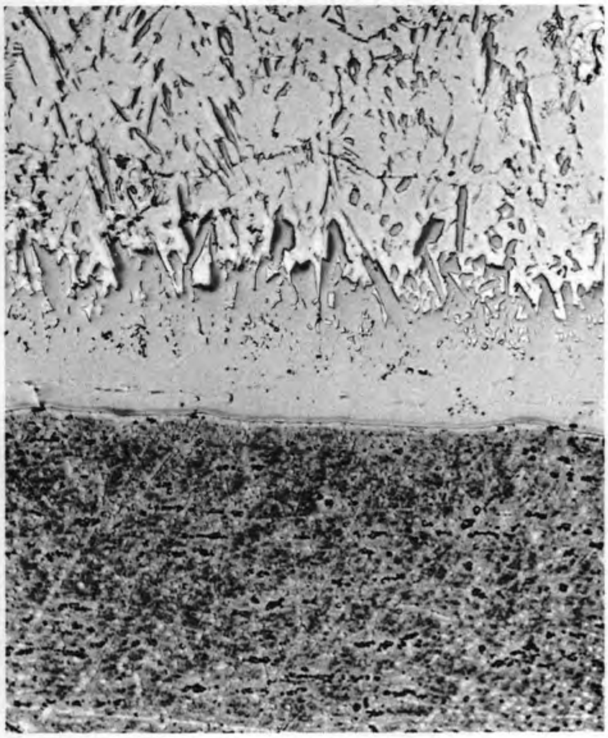
--52 S Al Y-9843

Fig. 9. Appearance of the Diffusion Layer Between 52 S Aluminum (upper portion of photograph) and Thorium After Four Hours at 600°C.
Unetched 100X

--Diffusion Layer

--Th

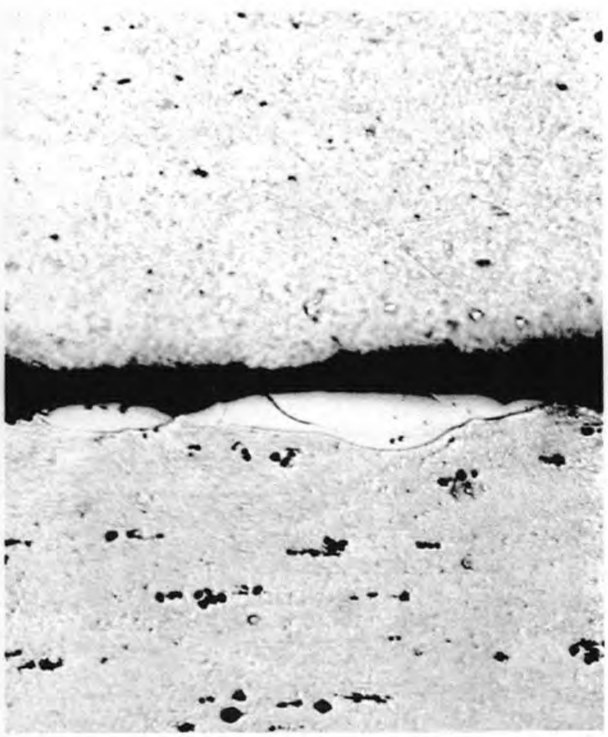
[redacted]



-52 S Al Y-9841

Fig. 10. Appearance of the Diffusion Layer Formed Between Aluminum 52 S Aluminum (upper portion of photograph) and Thorium After Four Hours at 600°C.
Unetched 100X

-Th



-SAP Y-9852

Fig. 11. Appearance of the Diffusion Layer Formed Between Sintered Aluminum Powder (upper portion of photograph) and Thorium After Four Hours at 500°C.
Unetched 250X

-Th

[redacted]

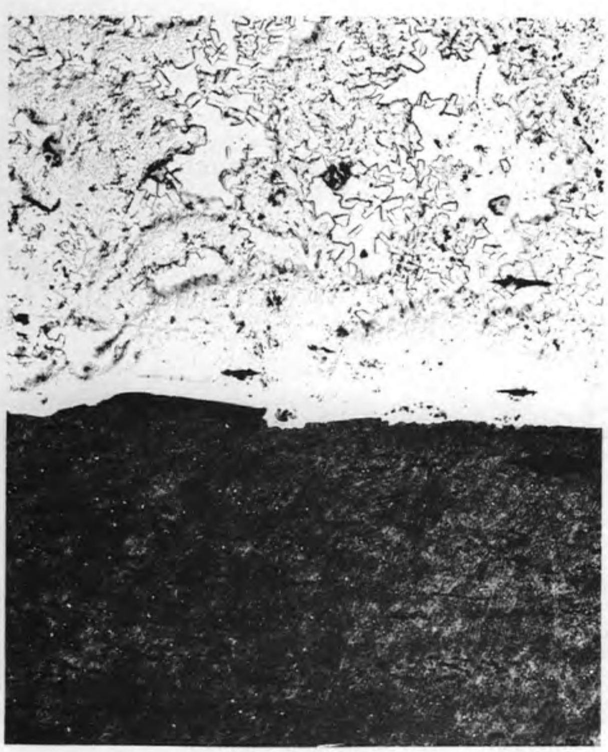
-Mg

-Diffusion
Layer

-Th

Y-9837

Fig. 12. Appearance of the Diffusion Layer Formed Between Magnesium and Thorium (lower portion of the photograph) After Four Hours at 500°C.
Unetched 250X



-Mg

-Th

Y-9835

Fig. 13. Appearance of the Diffusion Product Formed Between Aluminum-Magnesium and Thorium (lower portion of photograph) After Four Hours at 500°C.
Unetched 250X

-Al

-Diffusion
Layer

-Ni

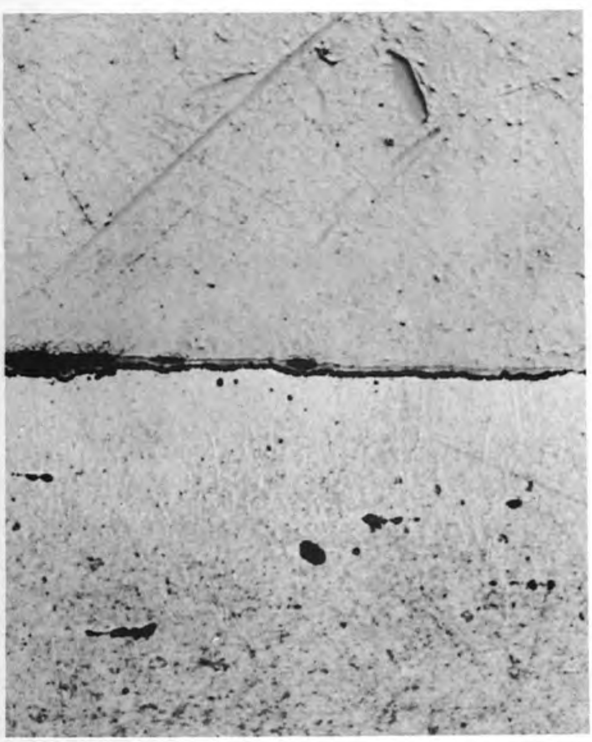
-Diffusion
Layer

-Th

Y-9840

Fig. 14. Appearance of the Diffusion Product Formed Between Aluminum-Nickel and Thorium (lower portion of the photograph) After Four Hours at 600°C.

Unetched 100X



Y-9879

Fig. 15. Appearance of the Diffusion Layer Formed Between Zirconium and Thorium (lower portion of photograph) After Four Hours at 700°C.

Unetched 500X

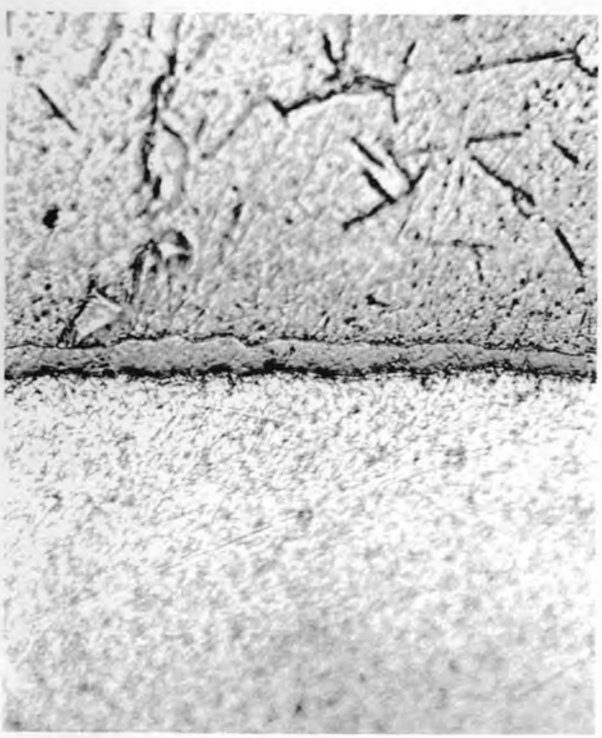
-Ti

-Th

Y-9853

Fig. 16. Extent of Diffusion Observed Between Titanium and Thorium (lower portion of photograph) After Four Hours at 800°C.

Unetched 250X



-Ti

-Al

Y-9836

Fig. 17. Extent of Diffusion Observed Between Titanium and Aluminum (lower portion of the photograph) After Four Hours at 500°C.

Unetched 1000X

Y-9854

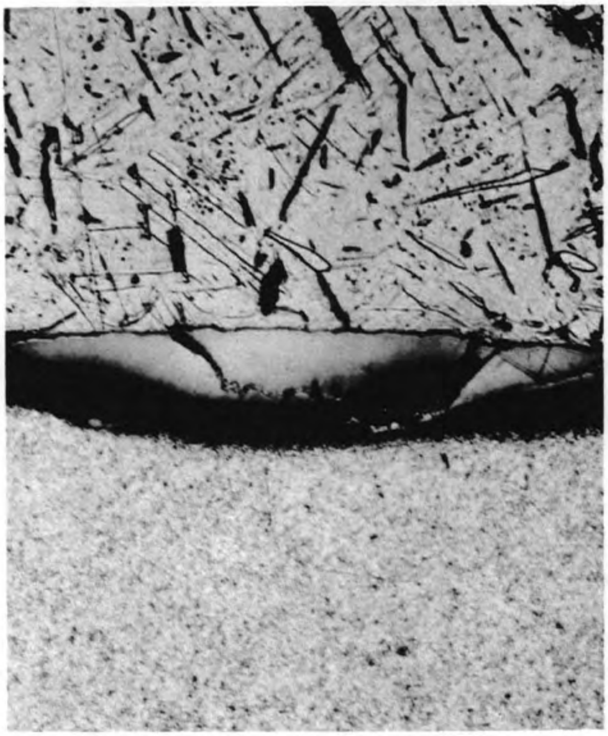


Fig. 18. Extent of Diffusion Observed Between Titanium and Aluminum (lower portion of the photograph) After Four Hours at 600°C.

Etched in HF 250X

Y-9880

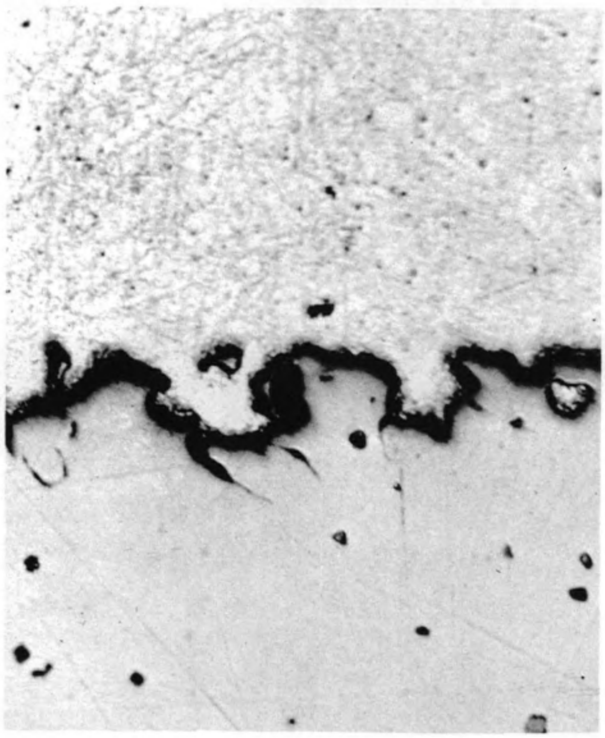


Fig. 19. Absence of a Diffusion Layer in the Couple Uranium-Magnesium After 16 Hours at 600°C.

Unetched 500X

[redacted]

APPENDIX C

Diffusion characteristics were investigated between uranium and magnesium, because no information was available on such a diffusion couple. (See Terminal Report on ORNL Slug Problem - Causes and Prevention, R. O. Williams, July 1950.) Diffusion couples were prepared from these two metals which were heated for: 4 fours at 400°C; 4, 32, and 64 hours at 500°C; 4, and 16 hours at 550°C; 4, 16, and 48 hours at 600°C. Upon miscroscopic examination, no evidence of diffusion could be found. These two metals are virtually insoluble in each other.

[redacted]

[redacted]

APPENDIX D

Solution for Cleaning of the Thorium Surfaces:

50 cc of HNO_3

48 cc of H_2O

2 cc of H_2SiF_6 (30% Strength)

Temperature Range - 50 to 80°C

Solution for Cleaning of the Aluminum and its Alloys:

20 grams of NaOH

80 cc of H_2O

Followed by a Rinse in 10% HCl Solution.

Solution for Cleaning Zirconium and Titanium:

46 cc of HNO_3

46 cc of H_2O

8 cc of HF (48% Strength)

Used at Room Temperature.

[redacted]