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SEP-102

UNITED STATES ATOMIC ENERGY COMMISSION

URANIUM-ALUMINUM DIFFUSION AND ASSOCIATED STUDIES

By
Samuel Storchheim
John Zambrow

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DATE 2/16/60

For The Atomic Energy Commission

H. R. Canale
Chief, Declassification Branch de

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ABSTRACT

During an investigation of the alloying of uranium and aluminum, aluminum was found to diffuse faster into uranium than vice versa. Increasing the pressure between uranium and aluminum during interaction increased the rate of penetration of UAl_3 into aluminum. Linearly increasing thickness of Al_2O_3 films placed between uranium and aluminum in reaction couples inhibited U-Al reaction in an exponential manner. In addition, Al-Si eutectic penetration into aluminum was observed to be less than for UAl_3 penetration into aluminum.

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I. INTRODUCTION

A point of importance involving the use of aluminum-jacketed uranium reactor fuel slugs in atomic pile reactors is the diffusion between the uranium and aluminum. It is felt that a better understanding of this phenomenon would be of aid in analyses of slug failures which occur in the piles.

Some quantitative information has been published regarding this uranium-aluminum interaction. One of the important investigations was made by D.W. Bareis^{(1)*}. Among his conclusions were:

- a. "The extent of the alloying reaction appeared to increase with increased pressure between the aluminum and uranium surfaces".
- b. "In the alloying reaction, the aluminum and uranium form UAl_3 . The uranium diffuses to the aluminum surface through the UAl_3 layer.
- c. "Anodization of the aluminum surface prevents the alloying reaction at 450°C and below".

Bareis also determined the temperature effect on the rate of alloy penetration into aluminum. However, he stated that only two direct measurements were used and suggested that many more data were needed to determine the relationship accurately. For comparative purposes, he also gave values for penetration into aluminum as taken from the Oak Ridge report by Williams⁽²⁾.

The object of this present report is to describe the results of a more detailed study regarding the reaction of aluminum not only with reguline uranium but also with fine-grained uranium as prepared by the hot-pressing powder metallurgy technique. Results will also be presented regarding an investigation made concerning the effect that various types and thicknesses of aluminum anodized coatings have upon subsequent uranium-aluminum reaction when placed between them⁽³⁾. In addition, a study made of the reaction of Al-Si with uranium and Al-Si with aluminum will be discussed. The Al-Si referred to is that presently used in Hanford fuel reactor slugs which acts as: a U-Al diffusion barrier, a U-Al bonding material and a corrosion protection agent.

* Numbers in brackets refer to corresponding numbers in the Bibliography at the end of this report.

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II. PROCEDURE

A. Types of Materials Used

Reguline, beta-treated uranium was used as a reaction component against 2S aluminum as well as hot-pressed powder metallurgy slugs against 2S aluminum. The primary difference between these two uranium materials was that the hot-pressed slugs were very fine grained, 5 to 10 microns in diameter, while the beta-treated slugs were about 150 to 200 microns in diameter. The relative purities of the two materials were similar, the hot-pressed material having slightly higher contents of nitrogen and iron and a somewhat lower silicon content. In addition, varying thicknesses of differently produced Al_2O_3 films were placed between the aluminum and reguline or hot-pressed uranium metals forming the reaction couples. This was done to determine the effect the thickness of the Al_2O_3 film had upon ultimate U-Al reaction rates.

To complete the experimental work, pie-shaped sections from the sleeve of a Hanford bonded slug having a 13% Si-Al eutectic alloy were reacted in a furnace under vacuum.

B. Description of the Apparatus* and Its Operation

The U-Al reaction couples were placed in an 18-4-1 high-speed tool steel die between two 18-4-1 punches. The die has an O.D. which was 3.255" and an I.D. which was 1.443". In addition, the die contained a 5/32" diameter thermocouple well in its wall. This well extended 3" down from the top of the die and was located 1/2" away from the die I.D. The bottom punch was 1" high, 1.440" in diameter and had a 5/32" diameter thermocouple well centrally located. This well extended from the bottom of the punch to within 1/8" of the top of the punch.

The top punch was 3" high with a 1.440" diameter and was solid. The die assembly fitted into the I.D. of a cylindrical Hevi-Duty ceramic heating furnace which in turn fitted into a water-cooled stainless steel pot. After the die and furnace were placed upright in the pot, the pot was sealed with a water-cooled cover.

* For further descriptive information regarding the apparatus used for the diffusion experiments of this report, see reports NYO-1129 by H.H. Hausner and N.P. Pinto, "Hot-Pressing of Uranium", June 16, 1950, and SEP-39 "High Density Uranium by Hot-Pressing" September 27, 1950.

I II. PROCEDURE (cont'd)

This cover contained a centrally located Wilson seal with an 18-4-1 punch, one inch in diameter and eight inches long, placed in it. After sealing, the pot was evacuated, the heating coil energized and controlled by means of a variac until both the thermocouples indicated the temperature desired. Once this was accomplished, pressure was applied for a predetermined length of time to the 1st punch through to the top punch and to the couple. When the time for keeping the couple under pressure elapsed, the pressure was released, the energizing coil current turned off and the assembly allowed to cool. After cooling, the die was removed from the pot and the reaction couple was ejected.

C. Reaction Couple Preparation

After preliminary investigations regarding reaction couple preparation, the following standard conditioning techniques were adopted:

1. Uranium Preparation

The uranium slugs used were first machined to 1.369" in diameter and 1/4" thick. Immediately prior to couple assembly, the slugs were abraded with 320 silicon carbide paper, producing clean, smooth surfaces on the slugs.

2. Bare Aluminum Preparation

Discs of 2S rolled aluminum rod were used which were machined to 3/16" thick and 1.369" in diameter. In addition, sleeves of impact extruded 2S aluminum were used to contain and line up the subsequent U-Al disc couples. These sleeves were 1.370" on their I.D., 1.438" on their O.D. and received the same treatment as the aluminum discs. This treatment involved:

- a. Degrease in acetone
- b. Immersion in 5% NaOH at 80°C for five minutes
- c. Immersion in 50% HNO₃ at room temperature for three minutes.
- d. Water rinse
- e. Dry in blast of gas.

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II. PROCEDURE (cont'd)

3. Anodized Aluminum Preparation

Al₂O₃ coatings were placed on discs and sleeves in the following manner:

- a. Made anodic at 6 volts for 10 seconds in Oakite No. 90 solution
- b. Rinsed
- c. Pickled in an acid bath at 80°C for 10 minutes
- d. Rinsed
- e. Anodized

The actual anodization* was carried out for varying lengths of time in a number of different type electrolytes including chromic acid, sulfuric acid and phosphoric acid. Anodization was also accomplished by means of immersion for different times in hot baths of either an Alrok or an Alumox solution.

The effect of varying the time of anodization in both type baths was to build up heavier Al₂O₃ coats on the aluminum. No satisfactory means was found for determining the actual thicknesses of these coats. Because of this, it was decided to use, as a criterion for Al₂O₃ film thickness measurements, the length of stay of the aluminum in its anodizing bath.

D. Reaction Couple Assembly

Couples were assembled in the following manner:

1. An aluminum disc was placed in an aluminum sleeve.
2. A 3/8" square piece of molybdenum strip was placed on the center of the aluminum disc. The strip was 0.003" thick.
3. One or two 0.015" diameter molybdenum wire turns were placed flat against the aluminum disc.

* See appendix for details of the anodization treatments.

II. PROCEDURE (cont'd)

4. A uranium slug was placed over the bottom aluminum disc and the molybdenum pieces.
5. Another square molybdenum piece was placed on the uranium plus another turn or two of molybdenum wire.
6. A second aluminum disc was placed on the uranium disc over the molybdenum pieces.

The molybdenum strips were used as inert markers, since they did not react with either the uranium or the aluminum at the reaction temperatures used. In addition, they prevented U-Al interaction where they came between the uranium and the aluminum and thus acted as reference lines for eventual penetration measurements; i.e., the extent of penetration was measured from the U-Al interface, as defined by the molybdenum strip, up through and to the deepest penetration of the UAl_3 intermetallic compound formed. The molybdenum wires were used to determine whether the aluminum diffused faster into the uranium or vice-versa (the Kirkendall effect). This was accomplished by measurement of the distances between the wires after reaction.

E. Conditions for Reaction Studies

At first, reaction couples of bare aluminum to bare uranium were made by a hot-pressing technique and were then reacted in vacuo at various temperatures for different lengths of time.

The initial hot-pressing of these uranium-aluminum couples was carried out in vacuum at a temperature of 300°C under a pressure of 15 tons per square inch for a period of two minutes. This temperature was chosen as no incipient reaction occurred during hot-pressing between beta-treated reguline uranium and aluminum. When using uranium prepared by the hot-pressing technique of powder metallurgy, a slight reaction took place between the uranium and aluminum. The little that did occur was accounted for later in the study.

Since the ultimate penetration data obtained from these studies were so erratic, this method of preparation and reaction of couples was rejected. It was believed the results obtained were of no value because the aluminum expanded in part or in total away from the uranium during the reaction process. The extent of this U-Al parting depended upon the initial hot-pressed mechanical bond between the two. This in turn controlled the ensuing furnace reaction of the couples and in many cases actually prevented reaction.

II. PROCEDURE (cont'd)

It was, therefore, necessary to use another method for obtaining reliable data regarding the U-Al alloying process. To do this, the same hot-pressing technique was adopted; however, instead of reacting in a furnace at atmospheric pressure, the couples were reacted directly in the hot-pressing apparatus. This method was adopted after initial indications showed it to be satisfactory.

Temperatures used for alloying were 400°, 450°, 500° and 550°C. The reaction couples were pressed at a pressure of 11 tsi, which was maintained for two minutes.

Couples using varying thicknesses of Al₂O₃ films between the uranium and the aluminum were hot-pressed at 550°C for two minutes at 11 tsi. In addition, 9 tsi was used in another series of experiments.

(Pieces of the Hanford slug were furnace reacted in vacuo at 550°C for 20 hours, 500°C for 50 hours and at 400°C for 168 hours.)

F. Penetration Measurements and Methods of Calculating Penetration Constants

After a hot-pressed couple was ejected from the die, a quarter-pie-shaped section was cut from it, mounted and the maximum penetration into the aluminum discs was microscopically determined. Once these values were obtained, the penetration constants were calculated from the following formulae:

$$D = \frac{x^2}{t}$$

X = maximum penetration in cm.

t = time at reaction temperature in seconds.

D = penetration coefficient in cm²/sec.

$$t' = \frac{16.2 \times 10^{-7}}{D}$$

t' = time in hours to penetrate .030" of 2S Al

$$D = D_0 e^{-\frac{Q}{RT}}$$

Q = activation energy for penetration in cal/gm-atom

R = universal gas constant

T = absolute temperature of reaction

$$\ln D = \ln D_0 - \frac{Q}{RT}$$

D₀ = intercept on ln axis of ln D vs $\frac{1}{T}$ curve

II. PROCEDURE (cont'd)

A typical view of a quarter section of a couple after mounting may be seen in Fig. 1. Note the fiducial molybdenum wires and the molybdenum strips.

III. RESULTS

In studying the structures formed during U-Al alloying it was observed that typical penetrations were either of the triangular type, Fig. 2, and/or the irregular layer type, Fig. 3. As Bareis noted, there was a black layer between the aluminum and the main reaction product, UAl_3 . In addition, a greyish appearing constituent was found to exist either between the uranium and UAl_3 or else to extend from the uranium into the UAl_3 as thinning vein-like growths. The cracks seen in the UAl_3 of Fig. 3 indicate its brittleness.

A. Reguline Uranium vs. Aluminum

Bare, beta-treated reguline uranium vs bare 2S aluminum was reacted at various temperatures, for two minutes at 11 tsi. The results obtained were as follows:

<u>Reaction Temp., °C</u>	<u>D cm²/sec</u>	<u>t' hours</u>
550	30.0×10^{-7}	0.54
500	14.1×10^{-7}	1.15
450	15.9×10^{-7}	1.01
400	5.2×10^{-8}	31.0

$$Q = 29,400 \text{ cal/gm-atom}$$

$$D_0 = 4.1 \times 10^2 \text{ cm}^2/\text{sec.}$$

When reacted at 500°C for two minutes under a pressure of 9 tsi, the $D = 9.8 \times 10^{-7} \text{ cm}^2/\text{sec}$ and $t' = 1.64 \text{ hours}$.

B. Hot-Pressed Uranium vs. Aluminum

Hot-pressed powder metallurgy uranium slugs were reacted bare against bare 2S aluminum at the four different temperatures of above at 11 tsi for two minutes. The data obtained were:

Fig. 1 - View of a quarter section of a reacted U-Al couple showing fiducial Mo wires and Mo strips. Note the reaction product where direct U-Al contact occurred and the lack of interaction where the Mo strips prevented U-Al contact. Also observe how the Mo wires were pushed up into the Al away from the original U-Al interface as represented by the Mo strip-U interface.

Al

U

Unetched

500X

Fig. 2 - Typical triangular U-Al compound formation after reacting bare U against bare Al. In this case reaction was carried out at 450°C at 11 tsi for 2 minutes in vacuo.

Al

Reaction Zone
Primarily UAl_3

U

Unetched

500X

Fig. 3 - Typical irregular layer penetration zone obtained between U and Al after reacting in vacuo at 500°C under a pressure of 11 tsi held for 2 minutes. Note crack running horizontally through reaction zone and large amount of reaction product fanning out from the U side into the reaction zone. Also note black substance between Al and UAl_3 .

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III. RESULTS (cont'd)

<u>Reaction Temp. °C</u>	<u>D, cm²/sec</u>	<u>t', hours</u>
550	20.9×10^{-7}	0.77
500	88.4×10^{-8}	1.83
450	40.0×10^{-8}	4.04
400	14.6×10^{-8}	10.5

$$Q = 19,300 \text{ cal/gm-atom}$$

$$D_0 = 1.6 \times 10^1 \text{ cm}^2/\text{sec.}$$

C. Varying Thicknesses of Al₂O₃ Barrier Films between Uranium and Aluminum

As discussed before, varying thicknesses of differently produced Al₂O₃ films were placed between uranium and aluminum in reaction couples. The data regarding these couples including the calculated time to penetrate .030" of 2S aluminum at various temperatures, t', were as follows:

<u>Anodization Bath</u>	<u>Time in Bath, min.</u>	<u>Reaction Conditions</u>			<u>t', hrs.</u>	<u>U Type</u>
		<u>Temp. °C</u>	<u>Pressure, tsi</u>	<u>Time, min.</u>		
None	0	550	9	2	1.64	
None	0	550	11	2	0.54	Reguline
Chromic acid	5	550	11	2	1.95	Reguline
Chromic acid	10	550	11	2	3.3	Reguline
Chromic acid	15	550	11	2	5.8	Reguline
Chromic acid	15	550	9	2	3.5	Reguline
Chromic acid	30	550	11	2	∞	Reguline
Sulfuric acid	7.5	550	11	2	0.97	Reguline
Sulfuric acid	10	550	11	2	8.6	Reguline
Sulfuric acid	30	550	9	2	∞	Reguline
Alumox	1	550	9	2	3.4	Hot Pressed
Alumox	2.5	550	9	2	3.4	Hot Pressed
Alumox	15	550	9	2	55.0	Hot Pressed

III. RESULTS (cont'd)

D. Aluminum-Silicon Eutectic vs. Aluminum

Pieces of an as-received Hanford Al-Si canned slug were furnace reacted and the data obtained for the Al-Si eutectic penetration into the aluminum can were:

<u>Reaction Temp., °C</u>	<u>Time at Temperature, hours</u>	<u>D, cm²/sec</u>	<u>t',</u>
550	5	35.9×10^{-8}	4.50 hrs.
450	97	22.0×10^{-9}	73.5 hrs.
400	168	6.48×10^{-10}	104 days

$$Q = 49,500 \text{ cal/gm-atom}$$

$$D_0 = 6.8 \times 10^6 \text{ cm}^2/\text{sec}$$

Fig. 4 represents the as-received condition of the Hanford slug, while Fig. 5 represents an as-reacted condition of a piece of the Hanford slug.

E. Aluminum-Silicon Eutectic Intermetallic Compound vs. Uranium

Only Al-Si eutectic penetration constants into the aluminum were determined. This was caused by the fact that the uranium always fell away from the balance of the reacted piece and accurate penetration measurements were not feasible.

IV. DISCUSSION

A. Uranium-vs-Aluminum Reaction Couples

1. Effect of Temperature

For ease of comparison, $\ln D$ vs $\frac{1}{T}$ curves were plotted in Fig. 6, from the data of the uranium-vs-aluminum experiments. The curves were primarily of the straight-line type indicating that the data conformed to the equation

$$D = D_0 e^{-\frac{Q}{RT}}$$

HCl and Oxalic Acid Etched

200X

Fig. 4 - Hanford slug showing the as-received condition of the U-Al-Si Eutectic-Al interfaces.

U
Intermetallic
Compound
Void

Al-Si Eutectic

Al

Oxalic Acid Etched

200X

Fig. 5 - Hanford slug, U-Al-Si Eutectic-Al interfaces after being reacted at 400°C for 168 hours in vacuo.

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Fig. 6 Penetration as a function of temperature for reguline uranium into aluminum, hot-pressed uranium into aluminum, and Al-Si eutectic alloy into aluminum

IV. DISCUSSION (cont'd)

and that the activation energies of reaction calculated could be taken as representative of the penetration process investigated. In addition, it was seen from the straight-line curves produced that the process was temperature dependent in the manner that other penetration phenomenon were. Comparison with Bareis' data, see Table I-A, showed that both his activation energies and the values obtained for this report were reasonable and within fairly good agreement, this for bare uranium to bare aluminum reaction. It was noted that the curves for the hot-pressed uranium and reguline uranium were quite similar.

TABLE I
PENETRATION CONSTANTS OBTAINED WHEN ALLOYING

A. Bare Uranium to Bare 2S Aluminum

	<u>BNL*</u>	<u>ORNL*</u>	<u>Hot-Pressed U</u>	<u>Beta-Treated U</u>
D_0 (cm ² /sec)	1.1	1.9×10^{-4}	1.6×10^1	4.1×10^2
Q (cal/g-atom)	24,000	15,000	19,300	29,400

B. Aluminum-Silicon Eutectic to 2S Aluminum

D_0 (cm ² /sec	6.8×10^6
Q (cal/gm-atom)	49,500

* Data as obtained from D.W. Bareis' report(1).

2. Effect of Pressure

The effect of change in pressure was specifically noted when two couples using reguline uranium were reacted at 550°C for two minutes, one at a pressure of 11 tsi, the other at a pressure of 9 tsi. The rate of penetration for the 9 tsi pressed couple was lower than for the couple pressed at the higher pressure. In addition to this, it

IV. DISCUSSION (cont'd)

was observed in all the couples reacted under pressure, that penetration was considerably less extensive at the side U-Al interface than at the top or bottom interfaces. Since pressure along the sides of the reaction couple was always lower than that at the top and bottom interfaces, it appeared that Bareis' conclusion of increased pressure increasing the alloying reaction was true.

Bareis' remark that uranium diffused to the aluminum surface through the UAl_3 reaction layer would indicate that he was of the opinion that the uranium diffused faster into aluminum than vice versa. The relative results of the fiducial marker measurements indicated that aluminum actually diffused faster into the uranium than uranium into aluminum. The measurements always showed movement of the markers into the aluminum away from the uranium. Some actual marker movement values obtained for bare uranium to bare aluminum reaction were:

<u>Reaction Conditions</u>			<u>Movement of markers away from each other, cm</u>	<u>Type Uranium</u>
<u>Temp. °C</u>	<u>Pressure, tsi</u>	<u>Time, min.</u>		
550	11	2	0.010	Reguline
500	11	2	0.010	Reguline
550	11	2	0.015	Hot-Pressed
500	11	2	0.005	Hot-Pressed
400	11	2	0.005	Hot-Pressed

Possibly, the reason for the marker movement values not falling into a logical plot when graphed as a function of temperature was that the formation of the UAl_3 layer was irregular, Fig. 3. This was not only true of the experiments of this report, but also those of Bareis, and can be seen as well in Fig. 7 of his report. Thus, the tendency was for the molybdenum wires to move, but not necessarily in a manner which could be coordinated with movement in other diffusion couples. This would aid in explaining the apparent discrepancies in the data, e.g., the same amounts of movements for reguline uranium at temperatures of 550°C and 500°C and at 500°C and 400°C for hot-pressed uranium.

IV. DISCUSSION (cont'd)

B. Varying Thicknesses of Al₂O₃ Barrier Films

Parts of the data of Section III-C of this report, i.e., increasing Al₂O₃ thicknesses and time for uranium to penetrate through the Al₂O₃ film and through 0.030" of 2S aluminum were studied. These indicated that the U-Al interaction was inhibited very markedly with increasing time for the aluminum in the anodizing baths. It appeared that for a 15-minute time of anodization the sulfuric acid type Al₂O₃ film was most effective in preventing interaction, the alumox type was next most effective and the chromic acid type was the least effective.

Although the results of the bare uranium and aluminum penetration investigation showed increasing pressure caused increased penetration, the use of Al₂O₃ barrier films showed that decreasing the hot-pressing pressure tended to allow a greater amount of U-Al interaction. An explanation for this latter phenomenon would be as follows: The types of anodized films used for this work were known to be porous. Applying compressive forces to them caused them to be crushed and interlocking pore areas to be consolidated. The degree of pore area consolidation would control the resultant U-Al interaction, i.e., the greater the pressure, the greater the pore consolidation and the less the resultant U-Al alloying. In addition, the thicker the film, the less the pore continuity through it and thus the less the interaction for the uranium and aluminum. Should it be made thick enough, penetration through it would cease. This was found to be the case and was a confirmation of Bareis findings that an Al₂O₃ film placed between uranium and aluminum prevented their subsequent reaction.

The use of various thicknesses of phosphoric acid and Alrok type Al₂O₃ films as diffusion barriers was also attempted. However, generally erratic results were obtained with these films. This indicated that the films were not sufficiently continuous and/or reproducible in thickness to cause U-Al reaction to be inhibited in a systematic manner. Further work with these anodization treatments was, therefore, discontinued.

For a better understanding of the effect Al₂O₃ films had upon U-Al interaction, a typical view of partial Al₂O₃ film inhibition to hot-pressed uranium vs aluminum interaction is shown in Fig. 7. In this case, the Al₂O₃ film was produced by a 20-minute immersion in an Alrok anodizing bath. Observation should be made of the partial penetrations after reacting at 550°C in vacuo at a pressure of 9 tsi

IV. DISCUSSION (cont'd)

B. Varying Thicknesses of Al_2O_3

Barrier Films

Parts of the data of Section III-C of this report, i.e., increasing Al_2O_3 thicknesses and time for uranium to penetrate through the Al_2O_3 film and through 0.030" of 2S aluminum were studied. These indicated that the U-Al interaction was inhibited very markedly with increasing time for the aluminum in the anodizing baths. It appeared that for a 15-minute time of anodization the sulfuric acid type Al_2O_3 film was most effective in preventing interaction, the alumox type was next most effective and the chromic acid type was the least effective.

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IV. DISCUSSION (cont'd)

held for 2 minutes. In addition, note should be taken of the manner in which the Al_2O_3 was "pushed" back into the aluminum by the UAl_3 . This was another confirmation of the greater rate of aluminum diffusion into the uranium than vice-versa, i.e. the Kirkendall effect.

Fig. 8 is a view of the complete effectiveness a thick H_2SO_4 electrically produced Al_2O_3 film had in preventing U-Al interaction. In this case, the Al_2O_3 film was produced by holding the aluminum 30 minutes in the bath. The subsequent reaction couple was then hot-pressed in vacuo against hot-pressed uranium at a temperature of 500°C under a pressure of 9 tsi held for 2 minutes.

C. Aluminum-Silicon Eutectic Penetration into Aluminum

As with uranium vs. aluminum, a plot of $\ln D$ vs $\frac{1}{T}$ for Al-Si eutectic penetration into aluminum was a straight line, Fig. 6. This plot for the intermetallic layer penetration into aluminum indicated lower penetration coefficients, for the same temperatures, than for bare uranium vs. aluminum. Calculation also showed a higher activation energy for Al-Si eutectic penetration into aluminum than for uranium into aluminum, see Table I-B.

D. Aluminum-Silicon Eutectic Intermetallic Compound Penetration into Uranium

Unfortunately, as stated previously, the uranium always broke away from the Al-Si eutectic intermetallic layer after reaction and it was not possible to determine the extent of penetration between uranium and this layer.

V. SUMMARY

The following is a brief recapitulation of the findings of this report.

A. Uranium-Aluminum Alloying

1. Plots of $(\ln D \text{ vs } \frac{1}{T})$ for hot-pressed or reguline uranium vs. aluminum experimental penetration data were straight lines. The slopes of these lines gave reasonable activation energies for the process of penetration involved and agreed fairly well with previously published data.

U Heat Tinted 500X
 Fig. 7 - Al treated in Alrok anodizing solution then reacted against U in vacuo at 550°C at a pressure of 9 tsi held for 2 minutes. Several intermittent UAl_3 penetrations through the thin Al_2O_3 film may be noted. Also note how Al_2O_3 film is pushed back into the Al at these penetration points.

Unetched 500X
 Fig. 8 - Thick anodized layer formed on Al in H_2SO_4 electrolyte and reacted against U at 500°C under a pressure of 9 tsi held for 2 minutes. The Al_2O_3 film is unbroken and has prevented U-Al interaction.

V. SUMMARY (cont'd)

2. Increasing the pressure on a U-Al reaction couple during the reaction process caused the rate of penetration to increase.
3. Aluminum diffused into uranium faster than uranium diffused into aluminum.

B. Al₂O₃ Barrier Films Between Uranium and Aluminum

1. Increasing the thicknesses of Al₂O₃ films produced by the sulfuric acid, chromic acid or Alumox methods very rapidly decreased the rate of reaction of uranium and aluminum when placed between them. A sufficiently thick Al₂O₃ film completely prevented subsequent U-Al reaction.
2. Impervious films were obtained more rapidly with the sulfuric acid anodization method than with any of the others.
3. Phosphoric acid and Alrok type oxide films were not very effective in inhibiting U-Al alloying.
4. Increasing the pressure during the reaction process aided in preventing U-Al alloying.

C. Aluminum-Silicon Eutectic Reaction with Aluminum

1. Plotting $\ln D$ vs $\frac{1}{T}$ for Al-Si eutectic penetration into aluminum produced a straight line relationship.
2. The activation energy of the Al-Si eutectic-aluminum reaction was greater than that of uranium to aluminum while penetration coefficients were lower for the former than the latter for the same temperature of reaction.

D. Aluminum-Silicon Reaction with Uranium

It was not possible to determine with the techniques used the effect reactions conditions had upon Al-Si eutectic intermetallic compound vs. uranium interaction.

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VI. CONCLUSION

The results of this investigation should contribute to a better comprehension of the process of U-Al alloying and to the effect temperature and pressure have upon this phenomenon. The studies of the kinetics of the UAl_3 penetration into aluminum are important from the actual point of understanding and possibly preventing reactor slug failure.

Data obtained were reasonable and in fairly good agreement where similar data existed. In addition to obtaining data using reguline uranium, uranium formed by hot-pressing powder compacts was likewise investigated. When reacted against aluminum, slight differences in penetration rates between it and reguline uranium were found to exist.

A much better comprehension was obtained of the quantitative effectiveness Al_2O_3 diffusion barrier films had when placed between uranium and aluminum. Here the thickness of the films was varied as well as the methods of obtaining the films. Both were found to have an effect upon subsequent U-Al reaction.

Finally, Al-Si eutectic penetration into aluminum was also investigated and compared to U-Al penetration data.

APPENDIX

The technique used for obtaining Al_2O_3 film on a 2S aluminum specimen was as follows:

1. The aluminum was first made anodic at 6 volts in Oakite Precleaner #90 for 10 seconds. This was done to degrease and etch the aluminum surfaces.
2. Next the aluminum was pickled in an acid bath for 10 minutes with the bath being held at a temperature of 80°C . The bath itself was composed of $\text{CrO}_3 = 35$ gms/liter plus $\text{H}_2\text{SO}_4 = 176$ gms/liter.
3. The aluminum piece was then anodized in the particular bath desired.
4. After anodization, the aluminum oxide was sealed with steam.
5. Finally, the sealed piece was dried in an oven at 110°C for 30 minutes.

The actual anodization treatments were accomplished in the following manner:

I. ELECTROLYTIC BATHS

A. Chromic Acid Anodization

A stainless steel tank used to contain the electrolytic bath was made the cathode. The bath itself was composed of 100 gms/liter of CrO_3 held at $35 \pm 5^\circ\text{C}$. The starting voltage used was 5 volts which was increased to 40 volts after five minutes had elapsed. The specimen was anodized for the desired length of time after the 40 volts had been attained.

B. Sulfuric Acid Anodization

A glass tank containing a lead cathode was used to hold the electrolyte. The bath was composed of 84 gms/liter of H_2SO_4 , specific gravity of 1.84, held at a temperature of $25 \pm 5^\circ\text{C}$. The starting voltage was 5 volts which was increased to 18 volts after five minutes. The specimens were held for varying lengths of time after the 18 volts had been applied.

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APPENDIX (cont'd)

I. ELECTROLYTIC BATHS (cont'd)

C. Phosphoric Acid Anodization

A glass tank using a lead cathode was used to hold a bath containing 590 gms/liter of H_3PO_4 , 85%. Specimens were anodized in this bath for varying lengths of time at 20 volts.

II. IMMERSION BATHS

A. Alrok Bath

A glass tank was used to contain a bath made of 2.0% sodium carbonate plus 0.1% potassium dichromate. The bath was held at 65°C and the aluminum was immersed in it for varying lengths of time.

B. Alumox Bath

A glass tank was the containing vessel for the bath utilizing 30 gms/liter of commercially available Alumox salt. The bath was held at its boiling temperature while the aluminum specimens were immersed in it for varying lengths of time.

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