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APPLICATION OF METAL COATINGS ON URANIUM-SUMMARY REPORT

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UNITED STATES ATOMIC ENERGY COMMISSION

Application of Metal Coatings on Uranium

Summary Report

by

P. Chiotti, P. F. Woerner, H. H. Klepfer, K. J. Gill and R. E. Cutrell

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Application of Metal Coatings on Uranium

Summary Report

P. Chiotti, P. F. Woerner, H. H. Klepfer, K. J. Gill and R. E. Cutrell

Abstract

A number of procedures for applying metallic coatings to uranium were investigated. A number of tests were carried out in order to evaluate the coats obtained. The coating materials were tested in boiling distilled water and in some cases were further tested in 178°C water. Coated uranium samples were tested in boiling distilled water. Hot-press bonding conditions for bonding aluminum to the coating materials and to coated uranium were studied. In a number of cases the temperature dependence of the interpenetration rate between the coating material and uranium as well as between the coating material and aluminum were measured.

Coats of zinc, zinc-5 w/o aluminum, copper 9.7 w/o magnesium and magnesium were applied by the hot dip procedure. It was found that predipping the uranium for a few seconds in a fused salt bath consisting of KCl-LiCl eutectic (55.7 w/o KCl, 44.3 w/o LiCl, melting point 359°C) to which 10 to 20 w/o anhydrous ZnCl₂ is added promoted rapid and uniform wetting of the uranium by the molten metal bath. Smooth adherent coats one mil thick were obtained by centrifuging the hot coated specimens. Without centrifuging the coats varied in thickness from one to three mils. Magnesium coats were considered of questionable value due to the poor corrosion resistance of magnesium and the extremely weak and brittle nature of the bond formed between aluminum and magnesium. Zinc has much better corrosion resistance than magnesium in 178°C water and hot-press bonded Zn/Al couples show a tensile strength of as high as 7900 psi. However, diffusion of zinc along aluminum grain boundaries is rapid ($K = 4.2 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 200°C). The Cu-9.7 w/o Mg eutectic serves as an effective diffusion barrier between uranium and aluminum. This alloy has excellent corrosion resistance to 178°C water. One mil coats of this material were found to give effective protection to uranium against boiling distilled water for periods up to 100 hours. The alloy is quite hard (Rockwell C 24-27) but still forms a relatively strong bond with aluminum. Al/Cu-Mg couples pressed at 480°C for 10 minutes and at pressures

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of 16,000 to 30,000 psi gave tensile strength values ranging from 4640 to 7450 psi.

Diffusion coats of nickel, silicon and zirconium were produced on uranium by heating the uranium in a magnesium bath containing the desired metal in solution. Adhering bath material was removed with dilute acid and the alloy case formed was tested in boiling water. The nickel and silicon diffusion coats were found to give a fair degree of corrosion protection to the uranium. Diffusion coats approximately 0.3 mil thick offer effective protection to uranium in boiling water for periods of about 100 hours. The zirconium diffusion coats produced were found to be rapidly undercut by boiling water.

All of the above coats as well as one mil electroplates of copper, nickel, and chromium were found to be rapidly attacked by molten Al-Si eutectic.

Introduction

In cooperation with the efforts of the General Electric Company, Hanford Works, to reduce the frequency of fuel element failures in pile operation, the Ames Laboratory, at their request, has studied the application of corrosion resistant coats on uranium. One objective of the Hanford program has been to develop a thin metal coating for uranium fuel elements, or "slugs", which would serve as a secondary line of defense against water corrosion in the event of can failure. Qualitatively, the desirable properties such a coat should have are: high corrosion resistance to water in the temperature range of 160 to 200 °F, low capture cross-section for thermal neutrons; high ductility; high thermal conductivity; must form a strong metallurgical bond with uranium and Al-Si eutectic in order to insure high uniform thermal conductivity; should not form brittle intermetallic phases or compounds with uranium or Al-Si eutectic; should serve as an effective diffusion barrier between uranium and Al-Si eutectic; must withstand the Al-Si canning procedure; and must be economically feasible. Alternatives to this objective include the development of corrosion resistant coatings suitable for unbonded fuel element assemblies and corrosion resistant coatings which are suitable for the hot-press canning procedure developed at Hanford. In these two alternatives the requirements for a satisfactory coat are less restrictive, in that it need not withstand the action of molten aluminum-silicon eutectic. Recently emphasis has also been made on coats which, in the event of can failure, would retard rapid corrosion of the uranium for a sufficiently long period of time to permit detection of activity in the effluent water and discharge of the faulty slug before it can jam the pile tube.

The work done at Ames on the application and testing of metal coatings on uranium is summarized below. This material has been previously reported in reports ISC-287, 314, 346, 389, 426, 452, 486, 532, 576, 609, and 641.

The various methods commonly employed in the application of metallic coatings to metals may be classified as follows: electroplating, chemical reduction (electroless plating) and displacement reactions, hot dipping, cementation and diffusion, thermal decomposition of volatile compounds, condensation of metallic vapors, spraying, and cladding. These methods with the possible exception of "electroless" plating are well known and require no introduction. The "electroless" plating process is carried out in a solution containing a reducing agent and ions of the desired metal. The metal surface to be plated acts as the catalyst for the reduction reaction and the reduced metal ions bond to the metal surface to give a dense adherent plate (1,2,3). The formation of metallic deposits on metals by displacement reactions are well known, for example, the displacement of copper from aqueous solution by iron. Coats produced in this way often tend to be porous and non-adherent. However, similar reactions can be carried out in a fused salt bath at sufficiently high temperatures to obtain bonding or alloying of the displaced metal. Campbell (4) et al., describe a procedure for producing a dense chromium alloy coat on iron by heating it in a fused salt bath containing chromous chloride. The chromous chloride reacts with the iron to give an iron-chromium alloy and ferrous chloride.

All of these methods, with the possible exception of the "electroless" process, have at some time or other been used to coat uranium with varying degrees of success. The older work on coating uranium is summarized by Howe and Jones (5) and a bibliography covering the classified literature up to 1952 is given by Borgmier (6).

In this investigation the principal emphasis has been on dip-coating and diffusion-coating procedures although a limited amount of work was done on several other procedures. Some properties of the metals considered of interest in this investigation are given in Tables I, II, III, and IV. All the values given in Table I were taken from the published literature. The values given in Tables II, III and IV were determined in the course of this investigation, except as otherwise noted. Considering the relative merits of these materials zinc and Cu-9.7 w/o Mg eutectic were considered of particular interest. The excellent corrosion resistance of uranium-nickel alloys containing about 12 w/o nickel also suggests that nickel diffusion coats on uranium might be promising. Uranium-silicon alloys are known to have excellent corrosion resistance to boiling water and silicon diffusion coats were likewise considered of interest. Other diffusion coats were also studied.

Table I

Physical Properties of Some Metals of Interest in the Coating or Canning of Uranium

Metal	Cross-Section		Coefficient of Linear Thermal Ex- pansion near 20°C °C ⁻¹ x 10 ⁶	Thermal Conductiv- ity Near 20°C cal./cm. sec °C	Melting Point °C
	Barns*	Mils Equiva- lent to 30 mils of Al			
Al	0.22	30	23.9	0.53	660
Bi	0.015	432	13.3	0.020	2271
Cr	2.9	1.7	6.2	0.16	1890
Cu	3.6	1.3	16.5	0.94	1083
Fe	2.4	1.9	11.7	0.18	1539
Mg	0.07	156.0	26.0	0.38	650
Mo	2.4	2.6	4.9	0.35	2625
Nb	1.2	6.5	7.1	----	2415
Ni	4.5	1.0	13.3	0.22	1455
Pb	0.18	68.5	29.3	0.083	327
Si	0.1	58.2	1.6-4.1	0.20	1430
Sn	0.6	16.2	23.0	0.16	232
Zn	1.0	5.6	39.7**	0.27	419
Zr	0.4	50.6	5.0**	0.057	1850
U	---	-----	16.3***	0.064	1133

*Capture cross-section for thermal neutrons taken from Chart of the Nuclides, prepared by Knolls Atomic Power Laboratory, 3rd ed., 1950.

**For polycrystalline metal.

***Value obtained by taking one-third the value for the volume expansion of uranium.

Table II

Corrosion of Some Metals and Alloys in 100°C Distilled Water

Material	Time in Hours	Ave. Weight Change mg/cm ² /hr.	Remarks
Uranium ^a	----	-1.0 to -3.0	Black powdery surface, constant rate
U-5.1 w/o Cr	62	-0.60	Black powdery surface, pitted
U-17 w/o Ni	115	+5.0 x 10 ⁻³	Smooth black surface
U-11.3 w/o Ni	1326	+4.6 x 10 ⁻⁵	Smooth black surface
U-11.5 w/o Ni	1006	+2.0 x 10 ⁻⁴	Smooth black surface
U-87.9 w/o Zn	855	+1.05 x 10 ⁻³	Smooth black surface
Zinc	528	+0.03	Gray surface
Zinc	1320	+0.02	Gray surface
Al-12.5 w/o Si ^b	168	+2.14 x 10 ⁻³	
Al-12.5 w/o Si ^b	1008	+0.45 x 10 ⁻³	Passive after 4 weeks
Cu-9.7 w/o Mg	950	+2.08 x 10 ⁻⁵	Surface bright and untarnished
Mg-1.5 w/o Mn ^c	336	+0.042	

^aSee reference 9a, pp. 463-464^bSee reference 10, p. 50^cSee reference 14

Table III

Corrosion of Some Metals and Alloys in 178°C Distilled Water

Material	Time in Hours	Ave. Weight Change mg/cm ² hr.	Remarks
Uranium ^a	--	-139.0	
2S Aluminum ^b	16	+0.018	
Aluminum (commercially pure)	100	$+3.0 \times 10^{-3}$	Adherent coat
(commercially pure)	250	$+1.0 \times 10^{-3}$	Adherent coat
	800	$+3.0 \times 10^{-4}$	No pits evident
Cu-9.7 w/o Mg	283	-----	No measurable wt. change Surface bright and untarnished
Zinc	50	-0.63	Constant rate after 100 hours
	200	-0.57	
Magnesium	50	-----	6 gram samples, 10 cm ² surface, completely disintegrated
Dow AZ63	50	+4.0	Disintegrated at 100 hrs.
Dow AZ31	50	+4.0	Disintegrated at 100 hrs.
Dow AZ92	50	+3.0	Disintegrated at 100 hrs.
Mg-2Pb	24	-7.8	Badly corroded
Mg-6Pb	24	-9.7	Badly corroded
Mg-10Pb	24	-14.3	Badly corroded
Mg-2Al-2Sn	50	-0.2	
	100	-0.04	
Mg-5Al-5Sn	50	-1.0	
	150	-1.5	

^a See reference 5, pp. 185^b See reference 5, pp. 226

Table IV

Growth of Compound Layers (Diffusion Bands) for Various Metal Couples

Couple	k_o cm ² /sec.	Q cal/g-atom	Temp. °C	k cm ² /sec.
U/2S-Al ^a	4.1×10^2	29,400	200	$9.0 \times 10^{-12*}$
U/2S-Al ^a	1.9×10^{-4}	15,000	200	$12.0 \times 10^{-12*}$
U/2S-Al ^a	1.1	24,000	200	$7.76 \times 10^{-12*}$
Pwdr. Met. U/2S-Al ^a	1.6×10^1	19,300	200	$1.7 \times 10^{-8*}$
U/Al ^b	0.497	22,000	200	9.8×10^{-11}
			600	$1.3 \times 10^{-6*}$
U/Al-12.5 Si	-----	-----	600	6.0×10^{-7}
U/Al-12.5 Si ^c	-----	-----	600	8.4×10^{-7}
U/Al-13 Mg ₂ Si	-----	-----	600	1.8×10^{-6d}
			625	4.35×10^{-6}
U/Zn	6.1×10^3	35,000	200	$3.4 \times 10^{-13*}$
			600	9.4×10^{-6}
U/Zn-5Al	1.1×10^8	43,300	200	$2.0 \times 10^{-12*}$
			400	1.1×10^{-7}
U/Cu-9.7 Mg	1.32×10^{-6}	20,400	200	$2.0 \times 10^{-16*}$
			600	$5.5 \times 10^{-12*}$
			820	1.8×10^{-8}
U/Mg-35Ni	-----	-----	715	2.8×10^{-10}
U/Mg-4Si	-----	-----	715	2.0×10^{-9}
Al/Mg	-----	-----	430	1.1×10^{-8}
Al/Al-Mg eutectic ^e	1.5×10^2	38,500	440	3.3×10^{-10}
Al/Zn-5 Al	1.26×10^{-6}	7,490	200	4.2×10^{-10f}

*Extrapolated or calculated values

^aSee reference 15^bSee reference 16^cSee reference 10^dError in value reported in report ISC-486, pp. 9^eSee reference 17 for diffusion coefficients for aluminum couples^fGrain boundary diffusion of zinc into aluminum

Zinc coats and Cu-9.7 w/o Mg eutectic coats were applied to uranium by the hot-dip procedure. Diffusion coats of nickel, silicon and zirconium were produced by heating uranium in a molten magnesium bath containing the desired element in solution. Copper, nickel, and chromium plates were also applied by electro-deposition. The coats produced showed little promise as effective barriers between uranium and molten Al-Si. All of these coats were either dissolved or undercut by molten Al-Si eutectic at 600°C in a relatively short period of time. However, the properties of hot-dip zinc and Cu-9.7 w/o Mg coats indicate that they may be of interest in the production of unbonded or hot-press bonded fuel elements. The grain boundary diffusion of zinc into aluminum is relatively rapid as indicated by the penetration constant for the Al/Zn-5 Al couple given in Table IV. In this case a thin layer of lead between the zinc and aluminum should serve as an effective diffusion barrier. Lead is immiscible in either aluminum or zinc in the solid state and its corrosion resistance to 100 or 178°C water is good. Consequently, procedures for applying a thin lead coat to aluminum were studied.

Bonding conditions and bond strength for Al/Zn, Al/Cu-9.7 Mg and Al/Mg couples were evaluated. Other associated studies relative to these problems are also summarized in the following discussion.

Dip Coatings

Dip-Coating Uranium with Zinc

Several procedures were used in preparing the uranium surface for dip coating. Small specimens were polished on 240 grit silicon carbide paper, then degreased with trichloroethylene, followed by alternate treatments with 50% hydrochloric and 50% nitric acid solutions. The samples were rinsed with water and finally with acetone and dried. Degreased samples were also treated anodically in 40-50 w/o trichloroacetic acid, rinsed with water, treated with 50% nitric acid until clean, rinsed with water and acetone and dried. Another procedure involved anodic treatment in a solution consisting of sulfuric acid, glycerine and water in a volume ratio of 5:1:3 respectively. This treatment gives a bright smooth metallic surface.

In spite of great precautions in the preparation of the metal surface, consistent uniform wetting by the zinc bath was not always obtained. Failure to obtain complete wetting is believed to be due to partial oxidation or contamination of the uranium surface with oxide or other impurities as it is lowered into the molten bath. Oxides or other impurities usually form a film on the molten metal

bath or collect in the flux used on the bath. Consequently, as the metal samples are lowered into the bath, these impurities come into contact with the sample surface before it comes into contact with clean metal.

The most satisfactory procedure for obtaining rapid and uniform wetting of the uranium surface was found to be a pre-treatment of the uranium in a fused salt bath consisting of KCl-LiCl eutectic (55.7 w/o KCl, 44.3 w/o LiCl, melting point 359°C) to which approximately 20 w/o of anhydrous ZnCl_2 was added. Uranium dipped in this mixture at 400 to 450°C for a few seconds and immediately dipped in a molten metal bath is rapidly and uniformly wet by the molten metal. Elaborate surface preparations are unnecessary. Equally good results are obtained with uranium which is quite badly oxidized. In this case the uranium is left in the fused salt mixture for a few seconds after vigorous reaction between the uranium and salt are evident. Vigorous reaction sets in as soon as the metal surface reaches the fusion temperature of the salt mixture. The uranium oxide reacts with or dissolves in the bath and zinc is displaced by the uranium, some of which adheres to the uranium surface. However, the surface of the metal is relatively rough if the uranium is badly oxidized or if the metal remains in the salt flux for a prolonged period of time after it has attained the temperature of the flux. The thin layer of salt which adheres to the specimen when it is removed from the bath has a reddish brown color. The color is believed to be due to the presence of uranium trichloride.

In the case of a zinc bath, the flux can be placed on top of the bath and the surface preparation and coating can be combined in one operation. With the zinc bath at 450 to 475°C small samples can be coated in five to ten seconds without the formation of a measurable reaction or diffusion band at the zinc-uranium interface. Smooth and adherent zinc coats 1.0 to 1.5 mils thick were obtained on small samples by hot-dipping and then centrifuging to remove the excess zinc. Centrifuging was stopped and the samples were dropped into mineral oil or water while the zinc coat was still molten. In this way defects or thin spots in the coat due to points of contact between the samples and the centrifuge were eliminated by the action of surface tension before the coat solidified. Quenching in oil gave a smoother coat. The coats obtained in this manner are uniform in thickness except at sharp edges where the coats are somewhat thinner. The variation of the coat thickness at sharp edges can be reduced by rounding the edges prior to dipping.

The average weight loss for three uranium samples coated with zinc in this manner and tested in 100°C distilled water is given in Table V.

Table V

Corrosion of Zinc Coated Uranium in Boiling Distilled Water

Time Hours	Average Weight Loss mg/cm ²	Corrosion Rate mg/cm ² hr.
49	0.05	-0.0012
96	0.08	-0.00083
191	1.28	-0.0067
239	2.87	-0.012
313	9.94	-0.031

Pure zinc tested in boiling distilled water shows an average weight gain of 0.03 mg/cm² hr. after 528 hours and 0.02 mg/cm² hr. after 1320 hours. The weight loss obtained for the zinc-coated uranium samples is due principally to the development of surface pits. Consequently, the change in weight is due to the result of two processes, a gain in weight due to the formation of adherent corrosion products on the surface of the zinc and a weight loss due to pitting. The latter being predominant after 48 hours.

Since the pitted area is a small fraction of the total surface and assuming a weight gain of 0.02 mg/cm² hr. due to corrosion of the zinc, the weight loss due to pitting is of the order of 0.064 mg/cm² hr. after 313 hours. Pits form first at the edges of the samples and are visible after 48 hours. There is no evidence of undercutting of the coat at the points of failure. The zinc apparently offers effective anodic protection to the uranium.

Uranium forms only one compound with zinc. The rate of growth of the compound layer at the uranium-zinc interface at various temperatures below the melting point of zinc was measured. The rate of growth was found to follow the parabolic law

$$x^2 = kt$$

where x is the band width, t is the time and k is the rate constant, or penetration constant. The variation of k with temperature is shown in Figure 1. This variation can be described by an Arrhenius type equation

Figure 1. Temperature-Dependence of the Penetration Constant k for the U/Zn Couple.

$$k = k_0 e^{-Q/RT}$$

where Q has the value 35,000 cal/mole and k_0 is 6.1×10^3 cm²/sec. The extrapolated value of k at 200°C is 3.4×10^{-13} cm²/sec. This corresponds to the growth of a band 1.0 mil thick in seven months.

The compound formed does not adversely affect the corrosion resistance of zinc. An alloy containing 87.9 w/o zinc and 12.1 w/o uranium, consisting of the compound UZn₉ in an essentially pure zinc matrix, was tested in boiling distilled water. After 855 hours the average corrosion rate was 1.05×10^{-3} mg/cm² hr., which is a lower rate than was observed for pure zinc under the same conditions. The surface of the alloy showed no evidence of pitting or flaking and was smooth and black in color. A sample of an alloy containing 84.8 w/o zinc and 15.2 w/o uranium tested for 1006 hours in boiling water had much the same appearance as that of the above alloy.

These results were considered sufficiently encouraging to warrant an extension of the coating procedure to four-inch slugs. Cleaned slugs were dipped in a fused salt bath of KCl-LiCl eutectic containing 20 w/o ZnCl₂ at 525-540°C for about two minutes. As soon as the slug reached the temperature of the salt bath and reaction was evident it was removed and dipped in a zinc bath (50 pounds of zinc covered with KCl-LiCl flux) at 490-497°C for one minute. The slug was removed and dipped into a second zinc bath for a short period of time to remove adhering dross from the first bath. No flux was used on the second zinc bath and the surface was skimmed clean just prior to immersion of the slug. The slugs were given a final dip in a KCl-LiCl eutectic bath at 500-510°C, keeping the slugs in an upright position allowing the excess zinc to drain. Some of the zinc collected at the bottom end of the slug. The slug was then removed and shaken manually to remove, as much as possible, any excess zinc adhering to the bottom of the slug and dropped into a water or oil bath.

The tongs used to hold the slugs are shown in Figure 2 (a). These tongs make point contact with the ends of the slugs. The position of the grip-points were changed between zinc dips to insure complete wetting at the points of contact.

Although the work done was not sufficient to determine optimum conditions, fairly smooth and uniform coats were obtained. Measurements on the coated slugs indicate that the zinc coat varies from one to three mils in thickness. Since the zinc tends to collect at the bottom end of the slug during the dipping procedure, the coat at this end may be greater than three mils.

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(a) Iron Bar Tongs with Iron Points for Dipping 4" Uranium Slugs.

Angle Iron Bottom $\frac{1}{8}$ " thick, 1" sides, and $\frac{1}{2}$ " wide with Iron Ball Point

Iron Ring $\frac{1}{2}$ " wide, $\frac{1}{8}$ " wall, and $2\frac{1}{2}$ " O.D. with Iron Points.

(b) Angle Iron Holder or Rack for Dipping 4" Uranium Slugs in Molten Cu-9.7%Mg Eutectic

Figure 2. Tongs (a) and Rack (b) for Hot-Dipping Four-Inch Uranium Slugs.

A number of procedures were tried in an effort to obtain a more uniform coat.

In one procedure the hot coated slug was rolled down an inclined steel chute into a quenching bath. In another procedure the hot coated slug was placed on top of two rotating steel drums. In each case a more uniform coat was obtained at the ends of the slug; however, the side surface was partially roughened due to pickup of particles of metal thrown off by the rotating slug. Centrifuging may be a much more suitable procedure; however, suitable equipment was not available and no attempt was made to remove excess zinc from four inch slugs by this procedure.

A zinc-coated slug tested in boiling distilled water developed a few small pits after 24 hours. The appearance of the coated slug prior to testing and after 264 hours in boiling water is shown in Figure 3.

British investigators have also studied the problem of hot dip coating uranium slugs with zinc.⁷ Their results are in general agreement with the observations made in this investigation.

Dip-Coating Uranium with a Zinc-5 w/o Aluminum Eutectic

A number of four inch uranium slugs were dip coated with zinc-5 w/o aluminum eutectic by a procedure similar to that used to coat slugs with pure zinc. In this case the metal bath temperature was maintained at 410°C and the dipping time was one minute. The slugs were then dipped in a fused salt bath of KCl-LiCl eutectic at 450-475°C for one minute and then quenched in water. The coat was not as smooth as that obtained with pure zinc. Measurements made on the slugs before and after coating indicate that the coat is one to three mils thick.

The appearance of a coated four inch slug before and after corrosion testing is shown in Figure 4. Failure of the coat was by pitting.

The addition of aluminum to the zinc bath accelerates the rate of reaction of the bath with uranium. Data obtained on this couple indicate that the value of the penetration constant at 400°C is 1.1×10^{-7} cm²/sec. and is 2.0×10^{-12} at 200°C. These results show that the reaction rate is greater than that for uranium in contact with pure zinc. This increase in reaction rate is probably not too serious. However, the rate of diffusion of zinc along grain boundaries of aluminum is considerably more rapid. The aluminum grain boundary penetration constant for an Al/Zn-5 w/o Al couple was found to be of the order of 4.2×10^{-10} cm²/sec. at 200°C. Assuming the parabolic law holds for a penetration of up to

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(a)

(b)

Figure 3. (a) Zinc-Coated Slug. (b) Zinc-Coated Slug after 264 Hours in Boiling Distilled Water.

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(a)

(b)

Figure 4. (a) Uranium Slug Coated with Zn-5 w/o Al Alloy.
(b) Same Slug after 96 Hours in Boiling Distilled Water.

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10 mils, the time required to penetrate this distance for $k = 1.0 \times 10^{-10}$ is 74.67 days, and for $k = 1 \times 10^{-11}$, it is 2.04 years. It may therefore be concluded that any bonding material, which forms a diffusion couple with aluminum with k of the order of 1.0×10^{-10} cm²/sec at 200°C would very probably be unsatisfactory. A thin coat of lead between the aluminum and the zinc should serve as a good diffusion barrier. This possibility is described later.

Dip-Coating Uranium with Copper-9.7 w/o Magnesium Alloy

Copper forms a eutectic with magnesium at 9.7 w/o magnesium with a melting point of 722°C. This alloy has excellent corrosion resistance in 100 or 178°C water. A sample of this alloy tested in boiling water for 1000 hours showed no noticeable discoloration and a slight weight gain of the order of 3.0×10^{-5} mg/cm² hr. The same alloy after 283 hours in 178°C water showed no change in weight to within ± 1.0 mg and the surface remained bright and untarnished.

Small uranium samples (20 to 50 grams), predipped for a few seconds in a KCl-LiCl eutectic bath containing 10 to 20 w/o ZnCl₂ maintained at 400°C, were readily wet when dipped for 10 seconds in the copper-magnesium eutectic at 750°C. The metal bath is very fluid at this temperature and coats approximately 0.5 mil thick have been obtained without centrifuging. A number of these samples tested in boiling distilled water showed relatively little corrosion or pitting for the first 100 hours, but within the next 30 or 40 hours failed by pitting and undercutting. Coated samples showed an average weight loss ranging from 0.010 to 0.038 mg/cm² hr. after 132 hours. Considering the excellent corrosion resistance of the coating material, these results show that the coat obtained is imperfect. This is believed to be due to the adherence of oxide particles or other impurity particles to the surface of the metal during the coating operation, resulting in weak spots or imperfections in the metal coat. The impurities are apparently picked up from the fused salt on top of the bath or possibly from the metal bath itself.

The rate of reaction of uranium with the molten bath is not serious. Only an extremely thin compound layer is formed at the uranium interface during the dipping operation. The growth of this compound layer has been measured. At 820°C, the value of the penetration constant was found to be 1.8×10^{-8} cm²/sec. Values obtained for k at temperatures below the melting point of the bath are plotted in Figure 5. The value of k obtained at 820°C does not fall on the extrapolated curve of Figure 5 and is not shown on the plot. It was also noted that the growth of the compound layer began to deviate from the parabolic relation $x^2 = kt$ after prolonged heating at temperature. This effect may

Figure 5. Temperature-Dependence of the Penetration Constant k for the U/Cu-9.7 w/o Mg Couple.

be due to an increase in the concentration of magnesium at the interface which reduces the rate of growth of the compound layer. Magnesium does not form either compounds or solid solutions with uranium and the single diffusion band observed is believed to be the compound UCu_5 .

The value of Q obtained from the curve in Figure 5 is 20,400 cal/g-atom and k_0 is 1.32×10^{-6} cm²/sec. At 200°C, the extrapolated constant k is 2.0×10^{-16} cm²/sec. It may be concluded that the growth of the compound layer at this temperature is negligible.

The Cu-9.7 w/o Mg alloy is hard (Rockwell C 24-27) and rather brittle. Annealing this alloy at 400°C and 500°C for periods of 192 hours and 144 hours, respectively, has little effect on either the microstructure or hardness. Annealing in lead has a pronounced effect: The magnesium is rapidly replaced by lead to leave a soft copper-lead alloy with a hardness of Rockwell E 42-48 which compares favorably with the hardness of pure annealed copper. Alloy samples annealed for 24 and 48 hours in lead at 400°C showed that lead had penetrated to a depth of 0.208 cm. and 0.35 cm., respectively. These values give an approximate value of $k = 5.8 \times 10^{-7}$ cm²/sec. for the penetration constant. These results show that a one or two mil coat of the eutectic could be softened by dipping in lead at 400°C for a few minutes.

Chemical analysis of the soft copper-lead alloy formed gave 64.6 w/o copper, 33.1 w/o lead and 0.47 w/o magnesium. Although the analysis does not total 100%, it shows that most of the magnesium has been replaced by lead. Corrosion tests of this alloy in 178°C distilled water showed a weight gain of only 0.042 mg/cm² hr. after 572 hours. No pitting or flaking of the surface was observed; consequently, treatment of a Cu-9.7 w/o Mg alloy coat on uranium in lead should leave a highly ductile and corrosion resistant coat. However, penetration of the coat by lead would bring lead in close contact with uranium. Compounds formed by uranium and lead are very reactive toward water. Incomplete removal of the magnesium from the coat would be expected to give a magnesium-lead alloy which also has poor corrosion resistance to water. As little as 1.0 w/o magnesium in lead is reported to produce an alloy which is unstable in moist air. (See ASM Metals Handbook, 1948 ed. pp. 1226).

Annealing Cu-9.7 w/o Mg alloy in a bismuth bath at 400°C displaces the magnesium in much the same manner as annealing in lead.

Four inch uranium slugs were coated with the Cu-Mg eutectic by a procedure similar to that described for the application of zinc coats. In this case the sample holder (rack) shown in Figure 2 (b) was used since at the temperature of the Cu-9.7 w/o Mg bath (770°C), the steel tongs, Figure 2 (a), did not have sufficient stiffness or strength to permit a firm grip on the slug. The bath (approximately

30 pounds) was covered with a flux consisting of 50:50 mole % KCl-NaCl. The dipping time was two minutes in the KCl-LiCl-ZnCl₂ flux and one minute in the metal bath. The slugs were then removed, the excess metal shaken off manually, quenched in an oil bath until the coat had solidified, and finally quenched in water. A direct quench in water while the coat was still molten gave a rough surface. Due to the procedure used, some of the coat drained and froze on the bottom end of the slug to leave a much heavier coat than was desired. The coat on the side of the slugs was found to vary from about 1.0 to 2.5 mils. A more uniform coat could probably be obtained by use of a larger bath and by centrifuging the slug to remove excess material.

The appearance of a coated slug prior to and after corrosion testing is shown in Figure 6. Little or no corrosion or pitting was evident up to 72 hours in boiling distilled water. Pitting and undercutting of the coat were evident after 112 hours.

Dip-Coating Aluminum and Zinc with Lead

Since grain boundary diffusion of zinc in aluminum proceeds rather rapidly at relatively low temperatures (see Table IV), it may be undesirable to have zinc in direct contact with aluminum in an assembly for the corrosion protection of uranium. A thin layer of lead between the zinc and aluminum should provide a very effective diffusion barrier since lead is practically immiscible in either zinc or aluminum in the solid state. The Al-Pb and Zn-Pb systems show only limited solubility in the liquid state at temperatures near the melting points of the pure components. Therefore, attempts were made to apply a lead coat to aluminum and to zinc-coated uranium.

Aluminum is readily coated with lead by first dipping it for 30 seconds in a fused salt bath consisting of 20 to 30 w/o PbCl₂ and the balance KCl-LiCl eutectic at 450°C and then dipping in molten lead. The same flux containing a small amount of AlF₃, 1.0 to 3.0 w/o, was also found to be satisfactory. The lead coats obtained are well bonded but blister and separate from the aluminum after several hours in boiling water. Similar samples heated in a muffle furnace at 110°C for 19 days showed no tendency to blister or separate. Varying the lead bath temperature from 370 to 550°C or the addition of up to 10 w/o tin to the lead bath has little effect in reducing the tendency of the coat to blister in boiling water. The addition of zinc to the lead bath was considerably more effective; however, the coat still blistered and separated after 24 to 30 hours in boiling water. A flux consisting of roughly 15 w/o PbCl₂, 15 w/o ZnCl₂ and the balance KCl-LiCl eutectic is also effective in reducing the tendency of the lead coats to separate. A flux consisting of 30 w/o ZnCl₂ and the balance KCl-LiCl will promote wetting but likewise, does not prevent separation of the lead coat when tested in boiling water.

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Figure 6. (a) Uranium Slug Coated with Cu-9.7 w/o Mg Eutectic.
(b) Same Slug after 112 Hours in Boiling Distilled Water.

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In order to check possible corrosion effects when aluminum is in contact with lead, a small 2S aluminum can (3 inches long by 1 inch inside diameter) was filled with molten lead. A tight fitting aluminum cap was forced into the open end while the lead was still molten. Eight holes, 1/8-inch in diameter, were drilled through the side of the can. This assembly was tested in 178°C distilled water for 300 hours. After rinsing with acetone and thoroughly drying the assembly in a 100°C oven, the average weight gain was found to be 2.83×10^{-3} mg/cm² hr. This corrosion rate compares favorably with that obtained for commercially pure aluminum (see Table III). The inside and outside of the aluminum was coated with an adherent gray film. The lead showed only a slightly darkened surface. Galvanic effects do not appear to be a particularly serious problem.

Aluminum-lead-zinc sandwiches tested in 100°C water for 100 hours and in 178°C water for 100 hours showed separation of the aluminum-lead bond but no separation or undercutting of the lead-zinc bond.

Attempts to apply a lead coat over zinc-coated uranium (1.0 to 1.5 mil zinc coats) resulted in the dissolution of most of the zinc coat by the molten lead. Zinc forms a eutectic with lead containing 0.5 w/o zinc which melts at 318°C. Saturating the lead bath with zinc was only partially successful in preventing the zinc coat from dissolving in the lead. The lead bath temperature was varied from 340 to 385°C.

Diffusion Coating

Diffusion coats can be formed on the surface of uranium metal by soaking it in a molten magnesium bath containing the desired metal in solution. Magnesium does not form either solid solutions or compounds with uranium. Under favorable conditions the solute element diffuses into uranium and forms either a solid solution or one or more intermetallic phases depending on the relative activity of the solute in the magnesium bath and the uranium phases concerned.

Diffusion coats of nickel, silicon, and zirconium have been applied to uranium by this procedure. In each case the molten bath was contained in a MgO + 10 w/o CaF₂ crucible fitted inside a graphite crucible, and this combination was contained inside a stainless steel tube equipped with a water-cooled head and port so that samples could be introduced and removed from the bath. A small amount of KCl-LiCl eutectic flux was added to the bath; however, except in the case of the magnesium-nickel bath, the flux was too dense to float on top of the bath and the flux was not very effective in protecting the bath from atmospheric

oxidation. During prolonged soaking periods an inert atmosphere of helium or argon was maintained over the bath.

Although a number of procedures for surface preparation were tried in an effort to obtain uniform wetting of the uranium by the magnesium bath, the simplest and most effective procedure was to dip the specimens in a KCl-LiCl eutectic + 20 w/o ZnCl_2 flux at 400 to 450°C for a few seconds, just prior to dipping into the magnesium bath. Samples were held suspended in the bath in a small basket made from either tungsten, molybdenum, or tantalum wire. After dipping in the magnesium bath for the desired period of time, the samples were removed and quenched in water.

In order to test the corrosion resistance of the diffusion coat formed on the uranium, the adhering magnesium bath was removed with dilute nitric acid.

Nickel Diffusion Coats

The growth of the diffusion band on uranium dipped in a magnesium bath saturated with nickel at $715 \pm 15^\circ\text{C}$ is given in Table V. The initial rate of growth can be represented by the parabolic relation

$$x^2 = kt$$

where x is the thickness of the diffusion band or compound layer at time t and k is the penetration constant, but the rate of growth deviates from this relation for periods greater than about 60 minutes. An approximate value for the rate constant k for the initial growth period is $2.8 \times 10^{-10} \text{ cm}^2/\text{sec}$. The reason for deviation from the parabolic law for periods of time greater than 60 minutes is not known. However, microscopic examination indicates that cracking and scaling of the coat may be a limiting factor. It is interesting to compare the rate of growth of the compound layers in this case with that obtained for a solid U/Ni couple. Kittel (8) has studied the layer formation between various solid metal couples. He expresses the growth rate by the relation $x^n = Kt$. In the case of the uranium-nickel couple at 700°C , he obtains a value of $K = 1.0 \times 10^{-8} (\text{in.})^n/\text{day}$ and $n = 3$. Using this relation the time required to form a layer 0.4 mils thick is roughly 9.2 minutes, and for a layer 1.0 mil thick it is 2.4 hours. When compared with the values given in Table VI, these results indicate the initial growth of compound layers is somewhat more rapid in the solid U/Ni couple than in the solid uranium/liquid magnesium-nickel couple. The appearance of a nickel diffusion coat formed after 90 minutes in a magnesium-nickel bath at 730°C is shown in Figure 7.

Table VI

Diffusion Band Thickness on Uranium after Various Periods of Time
in a Mg-35 w/o Ni Bath

Bath Temp. °C	Time in Bath Min.	No. of Samples Measured	Average Diffusion- Band Thickness Mils
715	8	2	0.17
715	15	2	0.23
715	30	6	0.25
715	60	6	0.30
715	90	5	0.39
715	120	5	0.43
715	180	2	0.43
715	240	2	0.41

At temperatures above 738°C, the uranium reacts with the magnesium-nickel bath to form uranium-nickel eutectic which separates to form a liquid layer at the bottom of the bath. A sample of this material was analyzed and found to be 83.0 w/o uranium and 17.9 w/o nickel. The nickel content is somewhat greater than that of the uranium-nickel eutectic formed between the two compounds, U₆Ni and UNi. The results show that the alloy formed is essentially free from magnesium. This eutectic has excellent corrosion resistance to boiling distilled water. The corrosion rate after 115 hours was found to be + 0.005 mg/cm² hr. Two alloys of near eutectic composition prepared by arc melting showed only a slight weight gain after 1000 hours in boiling water (See Table II).

The results of corrosion tests made on a number of samples which were treated in a magnesium-nickel bath for varying periods of time are given in Table VII. Each sample was treated with dilute nitric acid to remove adhering bath material before corrosion testing. On exposure to boiling water, a smooth, dark to black, adherent layer forms on the surface. Little or no weight change takes place during the first 48 hours of exposure for

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Figure 7. Diffusion Coat Formed on Uranium after 90 Minutes in a Mg-Ni Bath at 730°C, Unetched. X250.

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Table VII

Dipping Conditions and Corrosion Resistance of Uranium Samples
Dipped in Mg-35 w/o Ni Bath for Various Periods of Time

Mg-35 w/o Ni Bath Temp. °C	Time in Mg-Ni Bath Minutes	Time in Boiling Water Hours	Average Weight Loss in mg/cm ² hr.
700	7	18	0.615
700	10	88	0.158
700	10	88	0.056
700	10	91	0.341
700	10	118	0.136
700	10	43	0.294
700	10	90	0.614
700	10	90	0.651
700	10	90	0.230
700	10	70	0.337
700	10	70	0.239
700	10	70	0.073
730	30	139	0.024
730	30	139	0.031
730	60	116	0.284
730	60	116	0.079
730	60	116	0.0157
730	90	116	0.088
730	105	165	0.094
730	120	156	0.022
730	120	142	0.084
730	120	142	0.046
730	240	139	0.200
730	240	139	0.242

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samples with a diffusion coat 0.30 mils or greater. After 72 hours, the average weight loss is of the order of $0.002 \text{ mg/cm}^2 \text{ hr.}$ Failure of the coat occurs at isolated points on the surface which spread quite rapidly, apparently by undercutting of the alloy coat. At the end of the testing periods indicated in Table VII, most of the coat was still intact and the weight loss was the result of failure of the coat at isolated patches on the surface.

The nickel diffusion coats are readily wet by molten zinc. A sample which had been dipped in a magnesium-nickel bath for 240 minutes at 730°C was cleaned with dilute nitric acid and dipped in a zinc bath at 500°C for two minutes, centrifuged and quenched. This sample, when tested in boiling water, showed a small weight gain after 200 hours, pits became evident after 275 hours, and at the end of 300 hours showed an average weight loss of $0.011 \text{ mg/cm}^2 \text{ hr.}$ The sample was sectioned and examined under the microscope. Much of the composite coat was still intact after the corrosion test. A photomicrograph of the coating is shown in Figure 8.

Silicon Diffusion Coats

Diffusion coats on uranium were also produced by dipping uranium into a magnesium bath saturated with silicon. The epsilon phase in the uranium-silicon system is known to have good corrosion resistance. A thin uniform coat of this material on uranium should give excellent corrosion protection; however, as in the case of the nickel diffusion coats the silicon diffusion coats contain weak spots and failure occurs at isolated areas on corrosion testing in boiling distilled water. The corrosion resistance of the silicon diffusion coats compare closely with the corrosion resistance of the nickel diffusion coats.

The rate of growth of a silicon diffusion band is more rapid than the rate of growth of a nickel diffusion band under the same conditions of time and temperature. The thickness of silicon diffusion coats produced after various periods of time at 715°C are given in Table VIII. The rate constant for the growth of the uranium-silicon compound layer is of the order of $2.0 \times 10^{-9} \text{ cm}^2/\text{sec.}$ at this temperature.

The diffusion coats tend to form around impurity particles on the metal surface as well as along deep cracks in the metal. Some areas of the coat show small discontinuities in the diffusion coat as shown in Figure 9. Figure 10 shows a uniform continuous coat formed in 45 minutes at 700°C .

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Figure 8 - Microstructure of a Zinc Dip Coat over a Nickel Diffusion Coat after 300 Hours in Boiling Water. Etched with HNO_3 -HF-Glycerine Solution, 250X.

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Table VIII

Diffusion Band Thickness on Uranium after Various Periods of Time
in Magnesium Bath Saturated with Silicon

Bath Temp. °C	Time in Bath Min.	No. of Samples Measured	Average Diffusion- Band Thickness Mils
715	15	2	0.27
715	15	4	0.59
715	30	4	0.71
715	45	4	0.92
715	75	2	0.76
715	90	1	0.83

Zirconium-Diffusion Coats

Zirconium is only sparingly soluble in magnesium at temperatures up to 900°C. The reported values for the solubility of zirconium in magnesium at this temperature vary, but, in general, is considered to be 1.0 w/o or less. Although this is a rather dilute solution, it was found possible to produce a zirconium diffusion coat on uranium by heating uranium in a magnesium bath containing excess zirconium. However, the rate of growth of a diffusion band is very slow even at temperatures as high as 950°C. Kittel's (8) measurements on the interdiffusion of solid uranium/zirconium couples show that the time required to produce a 0.1 mil coat at 700°C is of the order of 4.17 days.

Uranium samples heated in a magnesium bath saturated with zirconium at 950°C for 3 1/2 hours formed an alloy coat 1.45 mils thick. A very thin coat was also formed after one hour at 850°C. The quenched coat is rapidly undercut in boiling distilled water once the coat has failed. Failure in the samples tested occurred in 12 to 24 hours. In some cases the coat separated as patches of thin foil. Chemical analysis of this foil showed that it

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Figure 9 - Diffusion Layer Formed on Uranium Surface and along a Deep Crack after 15 Minutes in a Mg-Si Bath at 710°C, Etched with a Solution of 2 Parts H₂O Saturated with Potassium Tartrate and Sodium Fluosilicate to 1 Part Nitric Acid. X250.

Figure 10.- Diffusion Coat Formed on Uranium after 45 Minutes in a Mg-Si Bath at 700°C, Etched as Above. X250.

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contained as much as 20.0 w/o zirconium and no detectable amount of magnesium. These results were discouraging and no further work was done with this method of coating uranium.

Diffusion Coating by Heating Uranium in Contact with Metal Powders

An attempt was made to coat uranium by heating it in contact with chromium, zirconium or niobium powders in a rotating stainless steel tube. No suitable diffusion or cementation coat was obtained at temperatures up to 850°C after periods of time up to 8 hours. In each case the uranium surface was darkened, presumably by oxide and nitride, even though heating was carried out under a purified helium atmosphere. The source of these impurities was probably adsorbed gases released from the surfaces of the heating chamber and the metal powders as the system was heated. When uranium was heated in contact with chromium powder at 850°C, the powder and uranium reacted to form a eutectic.

This method might prove successful with more elaborate equipment whereby the system can be thoroughly outgassed before the uranium is introduced. The process could be carried out under a high vacuum and possibly with the addition of metal balls which would tend topeen the surface as the charge is rotated.

Electroplated Coatings

Electroplates of copper, nickel, chromium and many other metals have been applied to uranium. Plating procedures, and special procedures for preparing the uranium surface for plating are described in the literature (5,6,9). An exceptionally bright and clean surface is obtained by anodically etching uranium in a solution consisting of five parts sulfuric acid, three parts water and one part glycerine.

Nickel, copper, and chromium plates were applied to uranium using standard electroplating baths. These coats, as is already well known, are too porous to offer effective corrosion protection to uranium against boiling water. These electroplates were further tested in molten aluminum-silicon eutectic. It was hoped that they would effectively prevent or retard contact between the uranium and the aluminum-silicon eutectic and thus prevent or limit the growth of compound layers on the uranium surface. The results of these tests are described below.

Composite coats consisting of copper or chromium deposited on zinc-coated samples were also studied. A limited amount of work was done on composite coats of zinc-copper-chromium following procedures described by Beach and Faust (12) for plating composite copper-chromium coats over zinc coated beryllium.

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Zinc coats were applied by dipping uranium in a zinc bath at 475°C for one minute. The coated samples were centrifuged to remove excess zinc and then quenched in an oil bath. The quenched samples were rinsed in trichloroethylene and any surface stains were removed by light buffing or with dilute acid.

Electrodeposition of Copper on Zinc-Coated Uranium

Copper was plated on the zinc-coated samples in two steps. A cyanide bath was used to deposit an initial coat at a current density of 20 ma/cm² for 12 minutes. This coat was built up in a sulfate bath at about the same current density. The coat obtained was smooth and adherent.

The copper plates gave very little additional corrosion protection. Samples with a 1.0 mil copper plate over a 1.0 mil zinc coat, when tested in boiling distilled water, showed an average weight loss of 0.02 mg/cm² hr after 312 hours and 0.03 mg/cm² hr after 377 hours. This is roughly the same corrosion rates obtained on similar samples without the copper plate. Failure of the coat occurred at isolated points and by subsequent pitting.

Attempts to reduce the porosity of the coat by annealing revealed several interesting facts. The copper as plated contains a considerable quantity of adsorbed gas (presumably hydrogen) which causes blistering and separation of the copper plate from the zinc on rapid heating. By careful outgassing this can be prevented, but after heating for several hours at 300 to 400°C, a dark friable compound layer is formed under the copper plate. The copper plate can then be broken loose and separated from the sample. The formation of blisters and evolution of gas from pores in the plate can be observed visually by heating the samples in silicone oil (Dow Corning #703). Aging the samples for several days at room temperature greatly reduces the tendency toward gas evolution and blistering when the composite coat is heated. Blistering can be prevented in coats 0.6 mils or less in thickness simply by outgassing under vacuum for 15 hours at room temperature. Copper plates up to 2.3 mils thick were successfully outgassed by a similar treatment followed by heating at 100°C in a slow stream of helium for an additional 14 hours. Two of these samples were further heated to 425°C over a period of four hours, held at this temperature for a half hour, and furnace-cooled to room temperature. These samples showed no evidence of blistering.

Buffing with a wire wheel, however, did loosen and wrinkle the copper coat. The coat could then be cut and peeled from the uranium. The underside of the peeled coat was metallic gray with spots that were a yellow-brass color. Between this peeled coat and the sample was a fine black powder, evidently an intermetallic

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compound which had been shattered by the action of the buffing wheel. Enough of this black powder was collected to permit a Debye-Scherrer x-ray diffraction pattern to be taken. The pattern obtained could be indexed as simple cubic with $a_0 = 6.247 \text{ \AA}$. This excluded the possibility that the brittle phase responsible for bond failure might be UH_3 , UN , UO_2 or one of the Cu-Zn binary intermetallic phases. The amount of powder collected was not sufficient for chemical analysis; however, the compound is probably a ternary U-Zn-Cu compound. This possibility is supported by the fact that copper-plated zinc given the same heat treatment does not show this type of bond failure.

Measurements on the U/Zn couple show that a one mil coat is converted to a uranium-zinc compound in about two minutes at 425°C ; consequently, uranium had undoubtedly penetrated to the copper plate during the above heat treatment. Furthermore, zinc-coated uranium (zinc coat one mil or less in thickness) heated at 300°C for 60 hours in an inert atmosphere did not develop a bond or surface which could be readily powdered or cracked by severe buffing. However, zinc coats several mils thick given this treatment show a tendency to crack and separate at the zinc- UZn_9 interface.

Electrodeposition of Chromium on Zinc-Coated Uranium

Chromium deposited directly on zinc coated uranium gave little or no additional protection in boiling distilled water. These coats showed no pronounced tendency to blister when heated. However, annealing for several hours at 300°C gave a coat which was brittle and showed a tendency toward scaling. Kohler (13) points out that chromium plates on zinc are unsatisfactory, supposedly due to the formation of a dark-colored chromium-zinc phase between the chromium plate and zinc which results in subsequent peeling of the chromium. The use of a copper plate or flash coat between the zinc and chromium is reported to be advantageous. Copper and chromium plates were applied following procedures described by Beach and Faust (12).

These composite zinc-copper-chromium coats likewise show little or no additional corrosion protection. The results of corrosion tests of two of these composite coats and of a zinc dip coat are given in Table IX. Annealing these coats for several hours at 300°C resulted in the formation of a friable phase, presumably the same intermetallic phase responsible for the separation of Cu-Zn coats.

Table IX

Corrosion of Zn-Cu-Cr Coated Uranium in Boiling Distilled Water

Time in Hours	Weight Loss in mg/cm ²		
	1.2* Zn-0.5 Cu-0.3 Cr Coat	1.2 Zn-0.1 Cu-0.3 Cr Coat	1.2 Zn Coat
168	1.6	4.2	4.4
237	6.1	42.5	9.8
309	12	----	19.0

*Number preceding the chemical symbol gives the coat thickness of that metal in mils.

Behavior of Uranium and Coated Uranium in Molten Al-Si Eutectic

Uranium in contact with molten Al-12.5 w/o Si eutectic reacts to form brittle intermetallic phases. At 600°C, this reaction, after about 60 seconds results in the formation of alternate layers of intermetallic phases and eutectic. The formation of this structure at the U/Al-Si interface is due to the rapid growth of compound layers which crack or scale after attaining a thickness of approximately 2.4 mils and the subsequent penetration of the cracks by Al-Si. Measurement of the compound layer formed at 600 ± 5°C in periods of time ranging from six to 60 seconds show that the growth constant is of the order of 6.0×10^{-7} cm²/sec. This value is in good agreement with measurements ($k = 8.4 \times 10^{-7}$ cm²/sec.) made at Battelle (10). A sample dipped for one minute at 600°C showed some areas in which the compound layer was still intact while in other areas it had cracked and had been raised by the Al-Si as shown in Figure 11.

The possibility that the addition of small amounts of nickel, chromium, or magnesium to the bath might reduce the rate of reaction between the uranium and the bath was investigated. A bath having a nominal composition of five weight per cent nickel was prepared by adding nickel shot to an Al-Si bath. The bath was contained in a graphite crucible. This Al-Si-Ni bath, however,

Figure 11 - Uranium Surface after One Minute in Al-12.5 w/o Si at 600°C, Etched with 1% HF Solution. X250.

showed no pronounced decrease in its reactivity toward uranium over that of a bath with no nickel. Attempts to dissolve chromium in the bath at 600°C indicate that the bath dissolves less than 1.0 w/o chromium. This bath likewise showed little change in reactivity toward uranium. Magnesium is readily dissolved in the bath at 600°C. Two baths were prepared, one consisting of 81.6 w/o Al, 11.2 w/o Si, and 7.2 w/o Mg, and one consisting of 87.2 w/o Al, 4.7 w/o Si and 8.1 w/o Mg. The latter composition corresponds to 13 w/o Mg_2Si in aluminum. It was surprising to find that these baths were even more reactive toward uranium. The constant k for the Al-13 w/o Mg_2Si bath is of the order of $1.8 \times 10^{-6} \text{ cm}^2/\text{sec}$. while that for an Al-12.5 w/o Si bath is $6.0 \times 10^{-7} \text{ cm}^2/\text{sec}$. The increase in the rate of compound formation on the addition of magnesium was also observed by Cawthorne, et al. (10).

Uranium coats which are to serve as a secondary line of defense against corrosion failure of Al-Si canned slugs must withstand the Al-Si canning process. A number of coats prepared in this investigation were tested in an Al-12.5 w/o Si bath at 600°C. Previous work (11) has shown that electroplated copper,

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and nickel coats are too rapidly dissolved in a molten Al-Si bath to be of practical importance, and that chromium plates are the most resistant. These results are in agreement with the observations made on electroplated copper and nickel coats tested in this investigation. Chromium coats, one mil thick, showed little evidence of dissolution after two minutes in an Al-12.5 w/o Si bath at 600°C. However, the Al-Si penetrated weak spots in the plate and reacted with the underlying uranium to lift and undercut the chromium coat.

Nickel-diffusion coated and silicon-diffusion coated samples were also tested in an Al-Si bath at 600°C. The silicon-diffusion coat had little or no effect in retarding the reaction between the bath and the uranium. The nickel-diffusion coats were somewhat more resistant to the action of the bath. The nature of the reaction zone varied considerably among the various samples examined and along different areas of the same sample. This variation was probably due to cracks or weak spots in the coat and to variations in the wettability of the surface.

Hot-Press Bonding of Aluminum to Other Metals

Coats of zinc, copper-9.7 w/o magnesium, and nickel-diffusion coats are readily applied to uranium and have been shown to give a fair degree of corrosion protection against boiling water. These coats were considered of possible interest as a bonding material in the hot press canning procedure developed at Hanford. Therefore conditions for hot-press bonding aluminum to these materials were studied. A few experiments were also conducted on the hot-press bonding of aluminum to magnesium.

In these experiments, specimens in the form of sheet or thin flat sections having a surface area of two to three square inches were pressed together between stainless steel platens. These were heated by built-in Kanthal resistance elements.

Bonding Aluminum to Copper-9.7 w/o Magnesium Alloy

The results of hot-press bonding experiments on aluminum/copper-9.7 w/o magnesium couples are summarized in Table X. The bonds were evaluated qualitatively by microscopic examination and observing the ease of separating the bonded metals with a chisel.

The copper-magnesium alloy was prepared by adding copper to molten magnesium at 820°C under a helium atmosphere. The alloy was then furnace cooled to room temperature. Sections one-eighth inch thick were cut from the massive billet obtained and were

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Table X

Hot-Press Bonding of Aluminum to Copper-Magnesium Eutectic
(9.7 w/o Mg)

Temperature (°C)	Pressure (psi)	Time (min.)	Nature of Bond
470	8,000	5	Fair
470	8,000	10	Fair
475	11,000	15	Fair
475	15,000	20	Good
475	8,000	10	Fair
480	8,000	10	Fair
485	8,000	10	Fair
485	8,000	15	Good
490	8,000	10	Fair
490	12,000	10	Good
500	12,000	15	Good
500	8,000	10	Good
505	12,000	15	Good
510	8,000	10	Good
510	12,000	15	Excellent
515	8,000	10	Excellent
515	12,000	15	Excellent, fusion at inter- face
520	8,000	15	Excellent
520	12,000	15	Excessive fusion
520	8,000	10	Excellent
525	8,000	5	Excellent, limited fusion
525	8,000	10	Excellent, limited fusion
525	12,000	10	Excessive fusion
525	8,000	10	Marked fusion
530	8,000	5	Excessive fusion

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ground to give flat parallel surfaces. These specimens were then bonded to 30 mil 2S aluminum sheet. Surface preparations given these specimens prior to hot pressing are given below. Surface preparation for aluminum:

1. Dipped for 15 seconds in 15% KOH solution at 80°C.
2. Rinsed in water.
3. Dipped for 10 seconds in 10% nital.
4. Rinsed with water, acetone, and dried.

Surface preparation for Cu-Mg alloy

1. Polished on 180 grit wheel.
2. Degreased in benzene or trichloroethylene.
3. Rinsed with acetone.
4. Dipped in 10% nital for 15 seconds.
5. Rinsed with water, acetone, and dried.

Immediately after cleaning, the components were positioned in the press and pressure quickly applied to minimize oxidation of the contact surfaces.

Good bonding can be obtained at 475°C and 15,000 psi in 20 minutes. Good bonding can also be attained with lower pressure at higher temperatures; however, fusion at the interface sets in at 515°C. The occurrence of fusion is to some extent dependent on time and applied pressure. Once fusion sets in growth of the reaction region is very rapid and in some cases fusion occurred completely through the 30 mil aluminum. This is probably due to the formation of a ternary eutectic. The ternary eutectic Cu-33 w/o, Mg-7 w/o, and Al-60 w/o has a melting point of 507°C. The bond interface of a sample pressed at 12,000 psi, at 510°C for 15 minutes is shown in Figure 12. Evidence of fusion in a couple pressed at 12,000 psi at 515°C for 15 minutes is shown in Figure 13.

Considerably lower temperatures and pressures can be used to bring about bonding if a thin coat of zinc or tin is applied to the Cu-Mg alloy. These bonds are resistant to the action of 178°C water. Aluminum hot-press bonded to zinc-coated Cu-Mg eutectic at 380°C, 11,500 psi, for 15 minutes showed very little weight change and no indication of bond separation after 264 hours in 178°C water. Since zinc is not particularly resistant to 178°C water, it appears that the zinc in the bond interface must have alloyed with the other components. Composite Al/Sn/Cu-Mg bonds showed pronounced undercutting of the bond after 720 hours in 178°C water.

Aluminum was also hot-press bonded to uranium samples coated with Cu-9.7 w/o Mg eutectic. The conditions used and the results obtained are given in Table XI. A bond area obtained at 10,000 psi after 5 minutes at 525°C is shown in Figure 14.

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Figure 12 - Diffusion Bond Obtained at 510°C, and 12,000 Psi in 15 Minutes, 10% Nital Etch, 500X.

Figure 13 - Couple Pressed at 12,000 Psi for 15 Minutes at 515°C, Showing Evidence of Fusion in Bond Area, 10% Nital Etch, 500X.

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All the samples listed in Table XI, except the first and third samples, were thermal cycled from 450°C to 25°C. This was accomplished by dipping each sample in a fused KCl-LiCl bath at 450°C for twenty seconds followed by a water quench. Two to three cycles were sufficient to produce 10 to 15 small radial cracks per inch in the bond area. These cracks were perpendicular to the uranium interface and extended from the uranium, through the bond region, to the aluminum interface. However, the components were still firmly bonded after 12 cycles.

Table XI

Hot Press Bonding of Aluminum to Copper-9.7 w/o Magnesium Coated Uranium

Temperature °C	Pressure (psi)	Time (min.)	Nature of Bond Area
530	15,000	10	Excessive fusion
530	15,000	10	Fusion through eutectic layer
525	10,000	5	Limited fusion; excellent bond
515	15,000	10	Very good diffusion bond
515	10,000	10	Good diffusion bond
525	8,000	10	Excellent diffusion bond
525	8,000	5	Excellent diffusion bond
525	8,000	10	Good bond
515	15,000	15	Excellent diffusion bond

Specimens coated with Cu-Mg eutectic but not bonded to aluminum showed severe cracking and scaling after 24 cycles. Thin slabs of the Cu-Mg eutectic alone showed no cracks after the same number of cycles.

The coefficient of linear thermal expansion of the Cu-9.7 w/o Mg eutectic was measured over the temperature range of 0° to 40°C, by an interferometer method, and found to be $17.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. This

is somewhat less than the expansion coefficient of aluminum, and slightly greater than a mean value for the expansion of randomly oriented polycrystalline uranium (see Table I).

Bond Strength of Al/Cu-Mg Couples

Cylindrical specimens of aluminum and Cu-Mg eutectic were machined to one inch in diameter by 1-1/2 inches long. The ends of aluminum specimens to be bonded were machined to a small taper to insure some deformation of the metal. These ends were then cleaned by the procedures described above. The sides of the specimens were coated with a thin film of "Aqua Dag" (an aqueous suspension of graphite) to prevent bonding to the hot die. The couple to be bonded was then placed in a cold die so that the cleaned ends came in contact, the plunger was inserted and pressure applied. A resistance furnace was then placed around the die and the temperature raised to the desired temperature. Approximately 15 minutes was required to bring the die temperature to 480°C.

Figure 14 - Bond Interface of a Uranium Specimen Hot-Dip Coated with Cu-9.7 w/o Mg Eutectic and Hot-Press Bonded to Aluminum at 10,000 Psi, 525°C, for 5 Minutes, 10% Nital Etch, 500X.

After pressing for the desired period of time at temperature, the couple was removed and machined into tensile specimens. The over-all length of the couples was three inches. A two inch length extending one inch on each side of the junction was machined to 0.500 inches in diameter. Special grips were made to fit over the one inch diameter ends, and the tensile strength of the bond was measured in a standard tensile testing machine. The bonding conditions and strength of these couples are given in Table XII.

Table XII

Bonding Conditions and Tensile Strength of Al/Cu-Mg Eutectic Couples

Bonding Temp. (°C)	Bonding Pressure (psi)	Bonding Time (min.)	Ultimate Tensile Strength (psi)	Location of Failure
480	16,000	10	4850	Failed at bond
480	28,000	10	4650	Failed at bond
480	24,000	10	7450	Failed in Cu-Mg
480	30,000	15	6040	Failed at bond
480	20,000	10	4640	Failed at bond

Specimens were also prepared by placing the components in a hot die and then applying the necessary pressure. The bond strengths obtained showed considerable scatter, part of which was attributed to the formation of oxide films at the interface.

Hot-Press Bonding of Aluminum to Zinc

Thin sheets of 2S aluminum were hot-press bonded to zinc by the procedure described above. The zinc surface was prepared by using well known zinc etches. Two procedures were used, the first consisted of the following steps:

1. Dipped for 30 seconds in a 10% solution of HCl in alcohol,
2. Rinsed in water,
3. Dipped for 5 seconds in 10% nital to remove the film from step 1,
4. Rinsed with water, acetone, and dried.

The second procedure consisted of the following steps:

1. Dipped for 15 seconds in a solution of 200 g. CrO_3 and 15 g. Na_2SO_4 in 1000 ml of water,
2. Dipped for 10 seconds in a solution of 200 g. CrO_3 in 1000 ml of water,
3. Rinsed in water, acetone, and dried.

The latter procedure was considered preferable. Bonding conditions and results obtained are summarized in Table XIII.

Table XIII

Hot Press Bonding of Aluminum to Zinc

Zinc Surface Etchant	Pressure (psi)	Temperature ($^{\circ}\text{C}$)	Time (min)	Nature of Bond
10% HCl in alcohol	12,000	364	10	Poor
10% HCl in alcohol	12,000	364	15	Fair, but not uniform
10% HCl in alcohol	12,000	360	15	Fair, but not uniform
10% HCl in alcohol	12,000	362	5	Poor
10% HCl in alcohol	12,000	362	15	Poor
10% HCl in alcohol	26,000	362	5	Good
10% HCl in alcohol	16,000	362	5	Good
10% HCl in alcohol	16,000	362	10	Good
CrO_3 solution	12,000	375	5	Excellent, some melting*
CrO_3 solution	12,000	372	5	Excellent, no melting
CrO_3 solution	12,000	372	10	Excellent
CrO_3 solution	12,000	372	15	Excellent

*At temperatures near 382°C the couple forms liquid Zn-Al eutectic.

Bond Strength of Al/Zn Couples

Tensile test specimens of Al/Zn couples were prepared by the same general procedure described for the preparation of Al/Cu-Mg couples. The results of these tests are given in Table XIV.

Table XIV

Bonding Conditions and Tensile Strength of Al/Zn Couples

Bonding Temperature (°C)	Bonding Pressure (psi)	Bonding Time (min.)	Ultimate Tensile Strength (psi)	Location of Failure
380	30,300	10	5710	Failed at bond
380	34,900	10	1890	Failed at bond
380	34,900	15	7430	Failed in zinc
380	30,300	15	1900	Failed at bond
380	30,300	15	5370	Failed at bond
380	24,000	15	7900	Failed in zinc

Due to the restricted flow of the metals at the interface in the preparation of tensile specimens considerably higher pressures were required to obtain a good bond than were required in preparing well bonded flat specimens.

Hot-Press Bonding of Aluminum to Nickel-Diffusion Coated Uranium

A few experiments were conducted on the hot-press bonding of aluminum to uranium samples which had been diffusion-coated with nickel. The diffusion coats were applied by dipping the uranium in a Mg-Ni bath at 720°C for 30 minutes. The coated uranium samples were cleaned with dilute nitric acid. The aluminum surface was prepared as previously described. Samples were pressed at 15,000 psi at 575°C for times of 1, 2, and 10 minutes. The bond obtained was apparently strong. Microscopic examination showed the formation of an irregular diffusion band in each case. This effect might be reduced by pressing at lower temperatures; however, no further work was done with this couple.

Hot-Press Bonding of Aluminum to Magnesium

The magnesium was etched with 10% nital solution and the aluminum was prepared as described above. Bonding was obtained in 10 minutes at 410 to 435°C and at pressures ranging from 5,000 to 15,000 psi. Microscopic examination showed the formation of diffusion bands and what appeared to be a good bond. The bond was very brittle and friable and the components could be easily separated.

Conclusions

Zinc and copper-9.7 w/o magnesium eutectic coats approximately one mil thick have been successfully applied to uranium samples by dip-coating procedures. Diffusion coats of nickel and silicon have been produced on uranium by heating uranium in a molten magnesium bath containing the desired element in solution. All of these coats impart a fair degree of corrosion protection to uranium against boiling water. These coats as well as electroplates of copper, nickel, and chromium are not particularly effective in retarding the reaction of uranium with molten aluminum-12.5 w/o silicon eutectic.

The results of this investigation suggests several possibilities wherein some of these coats might prove useful. Diffusion coats of nickel and silicon, approximately 0.5 mil thick, give good corrosion protection to uranium in boiling water for periods up to 100 hours. Such coats may therefore prove useful as a second line of defense in unbonded fuel assemblies. The possibility that these coats might serve as a satisfactory base for hot-press bonded assemblies was not investigated sufficiently to permit any definite conclusions to be made. The procedure for applying these coats is simple, the principle disadvantage being the time required and the necessity of removing adhering bath material from the diffusion coat. The magnesium-nickel alloy is very reactive toward water and can be removed from the nickel diffusion coat simply by means of warm water or dilute nitric acid. Silicon does not adversely affect the corrosion resistance of magnesium and the Mg-Si coat may not be particularly undesirable in the case of an unbonded assembly. The Mg-Si coat would be undesirable in the case of a hot-press bonded assembly due to the extremely weak and brittle nature of the Al/Mg bond. The Mg-Si coat can be readily removed with dilute nitric acid.

Properties of the zinc dip coats indicate that they may also be of interest in unbonded assemblies but may be of questionable value for hot-press bonded assemblies due to the relatively rapid grain boundary diffusion of zinc in aluminum. The grain boundary

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diffusion can be prevented by the application of a thin lead coat to the aluminum. A lead coat can be applied to aluminum by the dip procedure described above.

Copper-9.7 w/o magnesium dip coats should prove useful in either bonded or unbonded fuel assemblies. This alloy forms an effective diffusion barrier between aluminum and uranium and has excellent corrosion resistance to 100°C or 178°C water. It is relatively hard but still has a fair degree of toughness.

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