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Corrosion Resistant Coatings for Uranium and Uranium Alloys

(Proposed for presentation at the 1977 NACE Meeting, being
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CORROSION RESISTANT COATINGS FOR URANIUM AND URANIUM ALLOYS

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ABSTRACT

This review paper considers coatings to prevent the corrosion of uranium and uranium alloys in two military applications: kinetic energy penetrators and aircraft counterweights. This study, which evaluated organic films and metallic coatings, demonstrated that the two most promising coatings are based on an electrodeposited nickel system and a galvanized zinc system.

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CORROSION RESISTANT COATINGS FOR URANIUM AND URANIUM ALLOYS*

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Introduction

The corrosion of uranium and uranium alloys in many applications is sufficiently fast to require protective coatings. The two major military applications of depleted uranium are kinetic energy penetrators and aircraft counterweights and ballasts. The penetrators are manufactured from depleted uranium with low alloying additions, primarily titanium. In the case of the penetrator, several potential problems are associated with corrosion of the uranium. First, a loss in weight caused by spalling corrosion products could result in a reduction in penetration. Second, corrosion product build-up or loss could cause a reduction in ballistic accuracy due to a shifting in the center of gravity of the penetrator. Third, corrosion product build-up and associated swelling of the encasement could cause the round to jam in the gun. Fourth, the entrance of hydrogen into the metal due to the corrosion reaction could embrittle the penetrator such that it would break-up either upon firing or when hitting the target. The penetrator designs vary considerably; in some, the uranium is completely bare and exposed, while in others it is completely encapsulated.

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The environments that the penetrators may be subjected to vary from storage in temperature and humidity controlled warehouses to exposure to salt spray. Thus, each round and the application of each round must be separately considered and tested before an accurate decision can be made as to whether a protective coating is necessary.

Presently, many counterweights and ballasts for aircraft are made from unalloyed depleted uranium. Most of this hardware has been coated with either paints or electroplated cadmium. Neither of these two coatings has proven to protect uranium adequately during service life. The resultant failure of the coating has allowed the spread of heavy metal and heavy metal oxides throughout the aircraft. This occurrence clearly presents a significant health hazard which must be corrected. In addition, the typical problems encountered when a piece of working hardware has a corrosion problem apply to this case as well.

As will be demonstrated, the most effective and economical coating for protecting uranium is a galvanized zinc or tin-zinc alloy. Before discussing these coatings and the other protection methods tested, a brief description is given of the mechanisms and magnitude of the corrosion response of uranium and uranium alloys.

Corrosion

Uranium Corrosion

Uranium metal exhibits a metallic lustre when freshly polished or cut; however, if left exposed to air an oxide film rapidly forms on the surface. The growth of this oxide film can be followed during its initial stages by observing the interference colors in light reflected from the materials surface. The color change sequence is: light gold, dark gold, golden brown, mauvish brown, mauve, blue mauve, blue black, and black.[1] This complete sequence occurs within a few days under normal laboratory conditions. If the uranium is exposed to more corrosive conditions, the initial growth of the oxide film is too rapid to observe the color changes.

The reaction of uranium with water vapor to form uranium dioxide and hydrogen gas,

$$U + 2H_2O \rightarrow UO_2 + 2H_2 \qquad (1)$$

has been studied by many investigators. Baker, et al.,[2] measured the amount of uranium reacted and hydrogen evolved as functions of water vapor pressure in an oxygen-free atmosphere. They found that both the reaction rate and the amount of hydrogen evolved increased with increasing water vapor pressure (Figure 1). They also observed[3] that when oxygen was added to the system, the corrosion rate was reduced by two orders of magnitude and no hydrogen was detected. As long as the oxygen was present, there was neither a net consumption of water nor an increase in hydrogen level. The oxygen, however, was consumed. By using O^{18} as a tracer, they found that the free oxygen combined with the released hydrogen to form water. Thus, the net reaction for uranium in the presence of water and oxygen is

$$U + O_2 \rightarrow UO_2 \tag{2}$$

They found little dependence of the reaction rate on either oxygen or water partial pressures when both were present.

Uranium Alloy Corrosion

Two major techniques have been used to study the corrosion of uranium alloys in moist environments: measuring the amount of hydrogen gas evolved during the reaction,* and measuring the weight gain from the amount of uranium dioxide produced during the reaction.

Magnani[4] tested several uranium alloys by measuring the amount of hydrogen generated during the reaction of the alloy with water vapor. Uranium alloy coupons were placed in glass vials filled with either water-saturated oxygen or water-saturated nitrogen and baked at 75°C for a predetermined number of days. The results of the hydrogen generation rate experiments in wet oxygen (Figure 2) show that, irrespective of the alloying elements, the rate of hydrogen generation generally decreases as the uranium content decreases. Compared to the wet oxygen tests, the results of the wet nitrogen tests (Figure 3) show significantly more scatter in the trend of decreasing hydrogen evolution with decreasing alloy content. The line drawn in Figure 3 is parallel with the line in Figure 2 but is displaced upwards by about a factor of four. Thus, the corrosion response of uranium alloys was affected by adding oxygen to the moist environment similarly to that of unalloyed uranium.

Weirick used a multiple-specimen thermogravimetric gas-flow apparatus to measure the weight gain of uranium and uranium alloys in moist air[5] and in moist nitrogen[6] environments at various temperatures and relative humidities. Figure 4 shows that a polished U-3/4 Ti sample exposed in air at 100°C and ten percent relative humidity experienced a corrosion rate of 7.6×10^{-4} mg/cm^2/hr, thirty times slower than that for the polished unalloyed uranium sample. Table I lists the corrosion rates of some lean

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*This method will lead to greater error as some of the H_2 is converted to UH_3 and not detected.

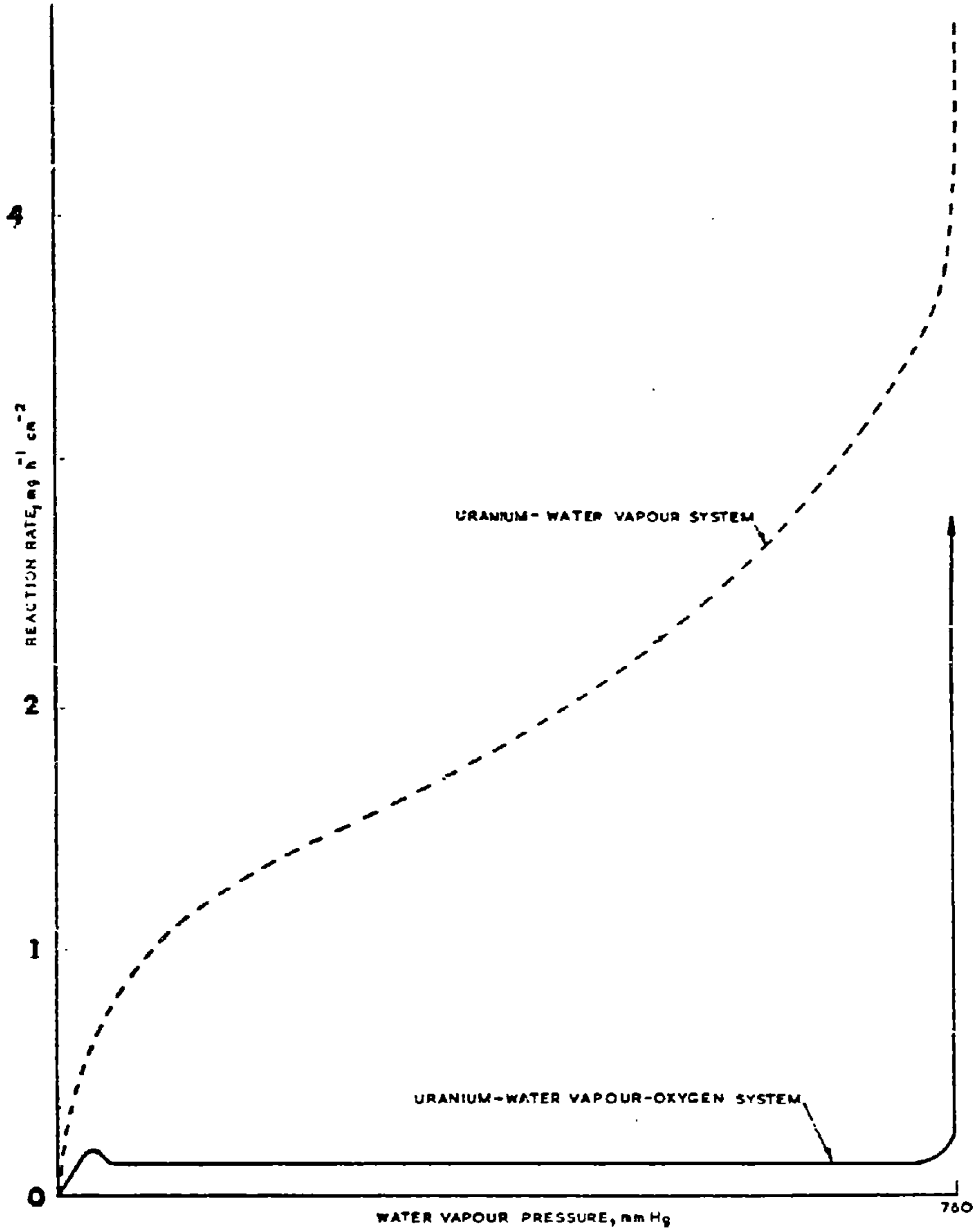


Figure 1. The Effect of Oxygen on the Dependence of Reaction Rate on Water Vapour Pressure

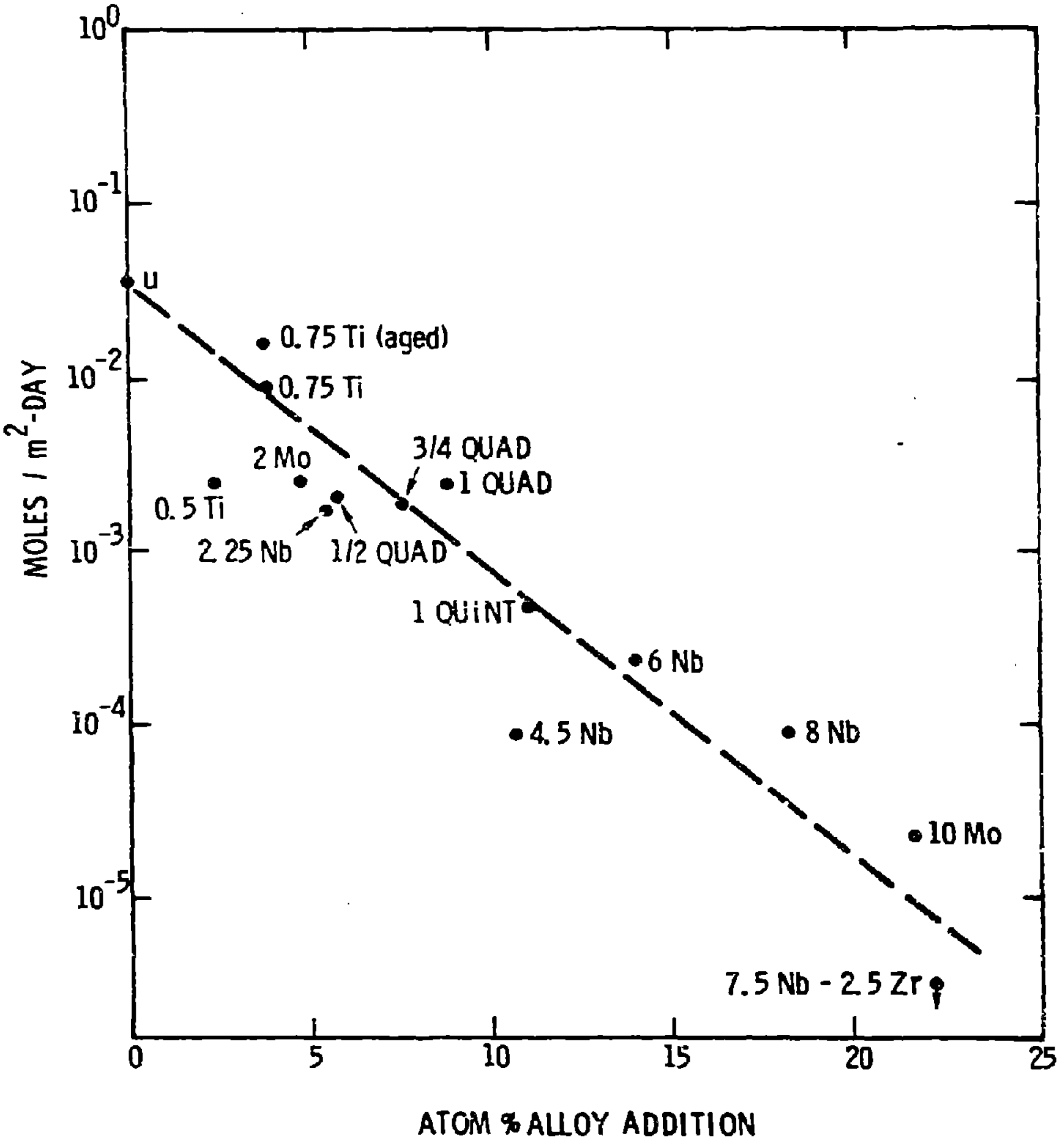


Figure 2. Rate of Hydrogen Production Versus Total Alloying Content for Uranium Alloys in Wet Oxygen at 75°C

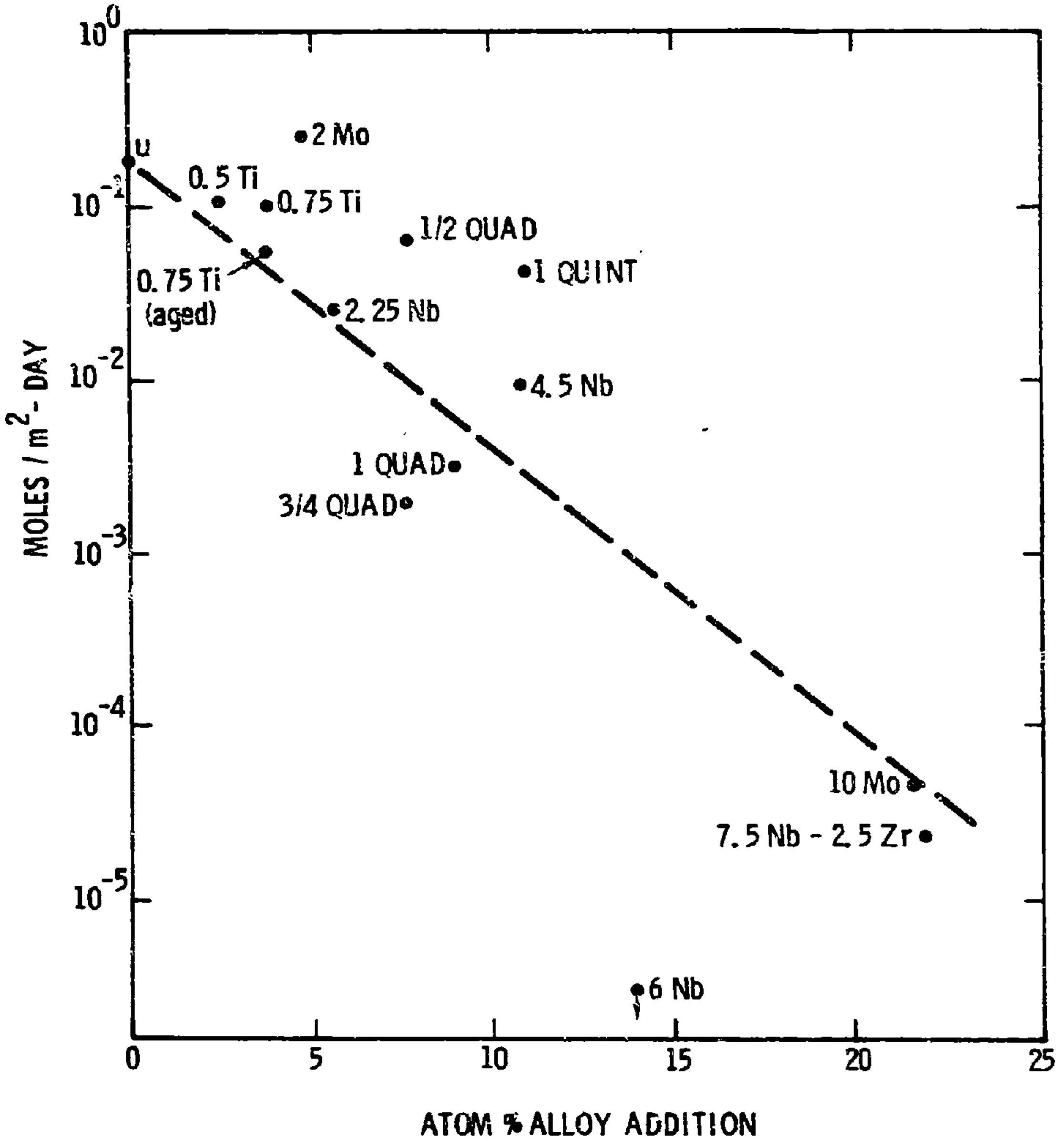


Figure 3. Rate of Hydrogen Production Versus Total Alloying Content for Uranium Alloys in Wet Nitrogen at 75°C

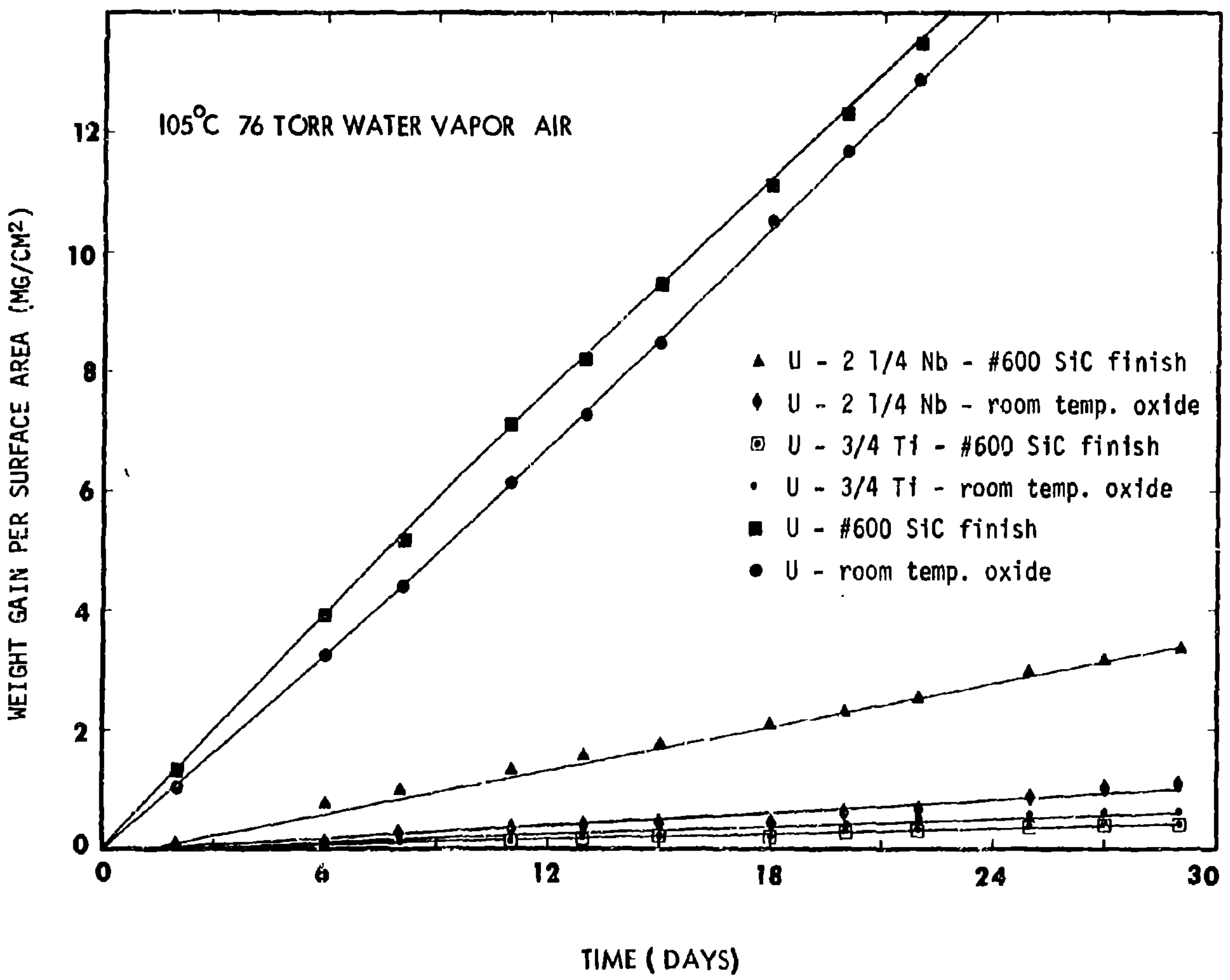


Figure 4. Relative Corrosion Resistance of U, U-3/4 Ti, and U-2 1/4 Nb in 10% R.H. Flowing Air at 105°C

TABLE I

CORROSION RATES OF LEAN URANIUM ALLOYS

Atmosphere	Corrosion Rate ($mg/cm^2/hr \times 10^{-4}$) U	3/4 Ti	2 Mo	2Nb
70°C				
50% R.H. Air		0.68		0.17
70% R.H. Air		0.75		0.23
90% R.H. Air		1.48		0.80
80°C				
50% R.H. Air		2.22		0.45
70% R.H. Air	~50.0	2.69	97.2	0.60
70°C				
50% R.H. N_2	-0.16	28.46	-1180.0	12.41
90% R.H. N_2*		1.65		1.49

*0.5% O_2

binary-uranium alloys as a function of the temperature, moisture content, and gas composition of the corrosion environment. The data show that, like unalloyed uranium in an oxygen-containing moist environment, the amount of moisture has a minimal effect on the corrosion response until saturation is approached, at which point the corrosion rate increases dramatically. Also like unalloyed uranium, as the oxygen content of the gas composition is reduced, the corrosion rate increases markedly. For a first-order chemical reaction with an activation energy near 30 kcal, the reaction rate would be expected to rise by a factor of 3.5 for every 10°C rise in temperature. This relationship was approximately followed by each material, with the exception of the polished U-2.2 Nb samples. The polished U-2.2 Nb material does not follow the pattern of decreasing corrosion susceptibility with increasing alloy content.

Coatings

Organic Films

It is doubtful that an organic coating can ever be found that will significantly protect unalloyed uranium. Considering the corrosion behavior of uncoated uranium, it is apparent that a coating must possess two essential properties:

a. a very low permeability to water vapor

b. a relatively high oxygen permeability

The latter property is a safeguard since it is accepted that no organic coating would be completely impermeable to water vapor. Orman and Walker[1] examined single and multiple coats of eleven paint systems that represent the three major curing mechanisms. None of these coatings were protective under the conditions of the test, and several were actively corrosive towards uranium. The major reason for failure of the organic coatings was that the water permeability rate of the coating materials was higher than the corrosion rates of the uranium. Furthermore, because the reaction rate is independent of water vapor pressure in the presence of oxygen, even a reduction in water vapor pressure at the uranium-coating interface has no effect until the level is reduced below about one percent relative humidity. They also found that, even with the addition of pigments with inhibiting characteristics, very little protection of uranium is offered by organic films.

It is well documented that zinc rich paints sacrificially protect ferrous substrates. A cursory evaluation was made at Sandia Laboratories, Livermore (SLL) by Johnson on the protection afforded to uranium and two uranium alloys by a zinc-rich inorganic paint. After the painted samples were exposed to moist nitrogen and salt fog, the paint was dissolved from the samples, the corrosion products removed, and the samples reweighed. As shown in Table II, the paint did provide some protection to all three materials in salt fog, but in moist nitrogen the corrosion rates for the painted and unpainted samples were essentially the same. The paint was destroyed on all samples tested.

Miller of Olin Corporation investigated the possibility of using organic films to protect the U-2 Mo alloy used in the U. S. Navy Phalanx program.[7] The three coating systems tried were a thermoplastic acrylic resin, a thermosetting acrylic resin, and a thermoset acrylic. The initial warm-water immersion tests demonstrated that only the thermosetting acrylic had any potential as a protective coating. However, further testing in 95 percent relative humidity (RH) air at 160°F showed that the coated penetrators corroded to the same extent as the uncoated penetrators. In all samples the coating was completely loosened from the surface of the penetrator by the end of seven days, and in most cases the coating adhered to the interior of the sabot when the projectiles were opened. Miller stated that apparently water that was transmitted through the coating initiated corrosion at the penetrator surface and the loose corrosion product then separated the coating from the penetrator body. These results demonstrated that organic films do not protect lean uranium alloys any more effectively than they protect unalloyed uranium.

Electrodeposited Coatings

Uranium is one of the more difficult metals to plate upon because its surface has a tendency to become passive. However, if the proper procedures are used, it is possible to obtain suitable mechanical adhesion between uranium and electrodeposited coatings. The most successful preparation techniques involve chemical or electrolytic treatment of the uranium in acid solutions containing chloride ions followed by removal of chloride reaction products in nitric acid. Uranium alloys are even more difficult to plate upon because the alloying elements (Ti, Mo, Zr, Nb) make the substrate material more resistant to the etchants used for preparing unalloyed uranium for plating.

Procedures have been developed at SLL for etching and plating uranium and uranium alloys (see Table III). Basically, the process consists of cleaning, pickling in nitric acid, etching in ferric chloride, removing the etchant reaction products in nitric acid, and then plating with nickel. During the etchant step, an average of one mil of metal is removed from the surface of parts. The ferric chloride etchant results in a relatively smooth etch, ~100 microinches, center-line average (CLA). Another possible etchant,

TABLE II
CORROSION RESULTS FROM ZINC PAINTED SPECIMENS

Results of Zinc Painted Specimens After 15 Days Exposure to Salt Fog Environment

Sample	Material	Surface Treatment	Weight Loss (mg)	Area (cm^2)	Corrosion Rate (mg/cm^2-day)	Remarks
S	U-Ti	As Machined	13,608	55	16.50	Control - Not Painted
1	U-Ti	Etched	677	55	0.82	Good Paint Adhesion
3	U-Ti	Etched	467	55	0.57	Good Paint Adhesion
B	U-Ti	Sandblasted	744	55	0.90	Fair Paint Adhesion
C	U-Ti	Sandblasted	376	55	0.46	Good Paint Adhesion
X	D-38	As Machined	22,766	50	30.50	Control - Not Painted
5	D-38	Etched	1,072	50	1.44	Good Paint Adhesion
6	D-38	Etched	5,085	50	6.75	Fair Paint Adhesion
E	D-38	Sandblasted	537	50	0.72	Poor Paint Adhesion
H	D-38	Sandblasted	1,163	50	1.55	Poor Paint Adhesion
U	Mulberry	As Machined	426	44	0.65	Control - Not Painted
I	Mulberry	Sandblasted	42	44	0.065	Good Paint Adhesion
K	Mulberry	Sandblasted	31	44	0.048	Good Paint Adhesion

Results of Zinc Plated Specimens After 15 Days Exposure to Moist Nitrogen Environment

Sample	Material	Surface Treatment	Weight Loss (mg)	Area (cm^2)	Corrosion Rate (mg/cm^2-day)	Remarks
1	U-Ti	As Machined	800	55	0.97	Control - Not Painted
2	U-Ti	Etched	781	55	0.945	No Paint Adhesion
4	U-Ti	Etched	771	55	0.94	"
A	U-Ti	Sandblasted	678	55	0.82	"
D	U-Ti	Sandblasted	607	55	0.74	"
7	D-38	Etched	5,157	50	6.88	"
8	D-38	Etched	5,168	50	6.88	"
W	D-38	As Machined	5,051	50	6.75	Control - Not Painted
F	D-38	Sandblasted	4,867	50	6.50	No Paint Adhesion
G	D-38	Sandblasted	4,846	50	6.50	"
V	Mulberry	As Machined	17	44	0.026	Control - Not Painted
J	Mulberry	Sandblasted	19	44	0.029	No Paint Adhesion

TABLE III

ETCHING AND PLATING PROCEDURES

1. Vapor degrease in trichloroethylene.
2. Caustic soak for 5 minutes at 70° to 80°C.
3. Water rinse.
4. Scrub surfaces with pumice.
5. Water rinse.
6. Pickle in 35 percent (by weight) solution of nitric acid at room temperature for 2 minutes.
7. Water rinse.
8. Etch 1400 g/l ferric chloride solution for 10-15 minutes at 55°C.
9. Water rinse.
10. Pickle in 35 percent (by weight) solution of nitric acid at room temperature for 2 minutes.
11. Water rinse.
12. Caustic soak for 5 minutes at 70° to 80°C.
13. Water rinse.
14. Pickle in 35 percent (by weight) solution of nitric acid at room temperature for 2 minutes.
15. Water rinse.
16. Plate in nickel sulfamate solution.

TABLE III (continued)

(Solution Composition and Operating Conditions)

Nickel Sulfamate Solution

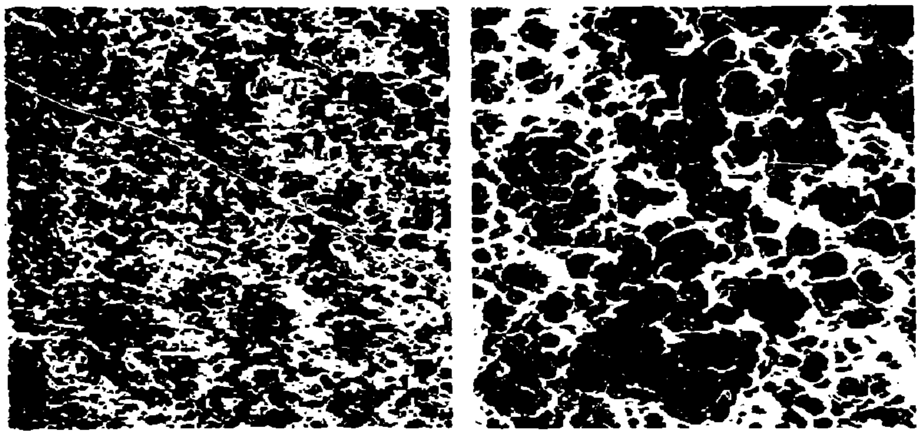
Nickel sulfamate	450 g/l
Boric acid	30 g/l
Surface tension	34-38 dynes/cm
pH	3.8 - 4.0
Temperature	48° to 50°C
Anodes	sulfur depolarized nickel
Filtration	continuous
Current density	270 A/m^2

zinc chloride, provides extremely rough surfaces (>400 microinches, CLA) and therefore offers more promise for applications in which joining dissimilar metals by plating is a consideration. Figure 5 shows a micrograph at the cross section of an etched uranium alloy part. It shows the much increased surface area with many sites for mechanical interlocking, or "interfingering," of the deposit. An added benefit of etching is that tunnels are obtained which subsequently fill with nickel plating, thus further enhancing adhesion. These etching effects are shown even more explicitly in the scanning electron photomicrographs in Figure 5. Nickel plate thicknesses of nominally 0.5 to 1.0 mil are typically deposited from a sulfamate solution as specified in Table III. Figure 6 is a micrograph showing the cross section of a uranium alloy part which had been plated with 0.5 mil of nickel. The analogous scanning electron photomicrograph is shown in Figure 7. The complete and uniform coverage of the uranium alloy substrate by the nickel is shown very clearly in these photographs.

Johnson, Dini, and Zehr[8] investigated the corrosion performance of various thicknesses of electroplated nickel coatings on uranium. Their specimens were etched in a ferric chloride solution and plated in a nickel sulfamate bath. The corrosion tests were done in moist nitrogen (2.8 percent H_2O, 97.2 percent N_2) at 70°C. The effectiveness of the coating was determined by measuring the amount of hydrogen generated during the corrosion tests. As shown in Table IV, increasing the nickel plating thickness does reduce the amount of corrosion, and concurrently, the amount of hydrogen generated. However, a nickel thickness of at least three mils was needed to produce a "pore-free" deposit.

The corrosion protection afforded to a uranium-3/4 titanium alloy by various metallic coatings and coating processes was evaluated by Weirick[5]. The metallic coatings considered were: electroplated nickel, electroplated cadmium, electroplated zinc, electroless nickel, ion-plated aluminum, ion-plated zinc, and a duplex coating of electroplated zinc over nickel with a zinc chromate finish. Moist air corrosion tests were performed in the previously mentioned MSTGA system. The test atmosphere chosen was air flowing at 1 liter/minute and maintained at 105°C and 10 percent RH. Any corrosion protection offered by a coating in this environment is due primarily to the physical integrity and uniformity of the coating and not to any beneficial sacrificial effects, i.e., anodic protection. The data of Figure 8 indicate that most of the coating materials performed in a satisfactory manner. The notable exceptions were the electroplated cadmium and zinc coatings and the ion-plated zinc. The reason for the poor performance was that coatings were incomplete, nonuniform, and nonadherent (see Figure 9).

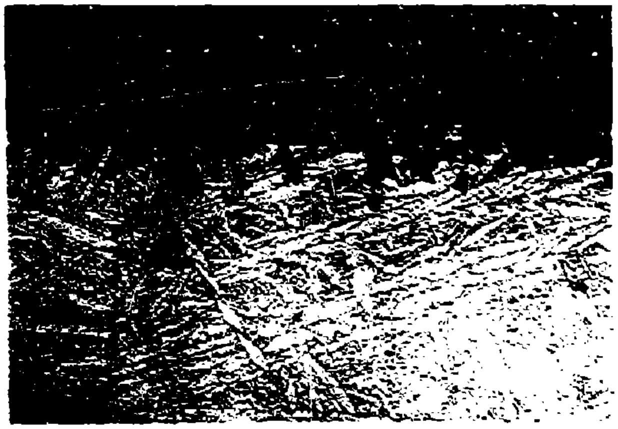
Dini and Johnson[9] have continued to explore alternate techniques of electroplating zinc onto U-3/4 Ti. Although they have succeeded in encapsulating samples with zinc, none of the techniques has produced a coating of minimal porosity and acceptable adherency. Thus, the electroplating of



300X

1000X

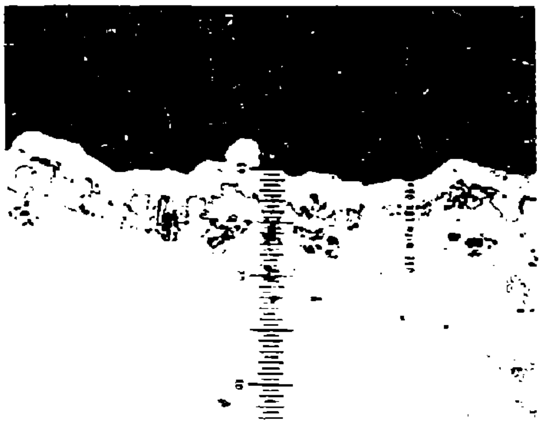
Surface Morphology



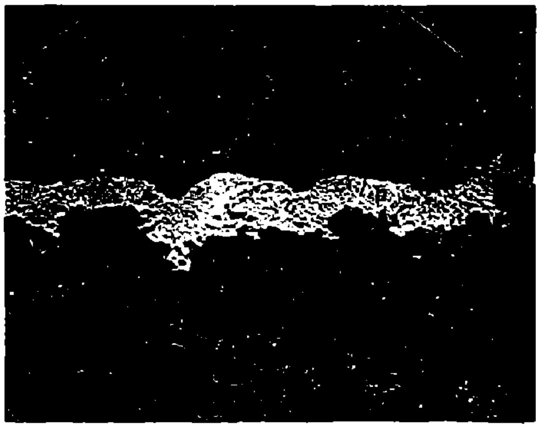
300X

Cross Section

Figure 5. Surface Morphology and Cross Section of U-0.75 Ti Showing Tunnels into Which "Roots" of the Nickel Plating Develop

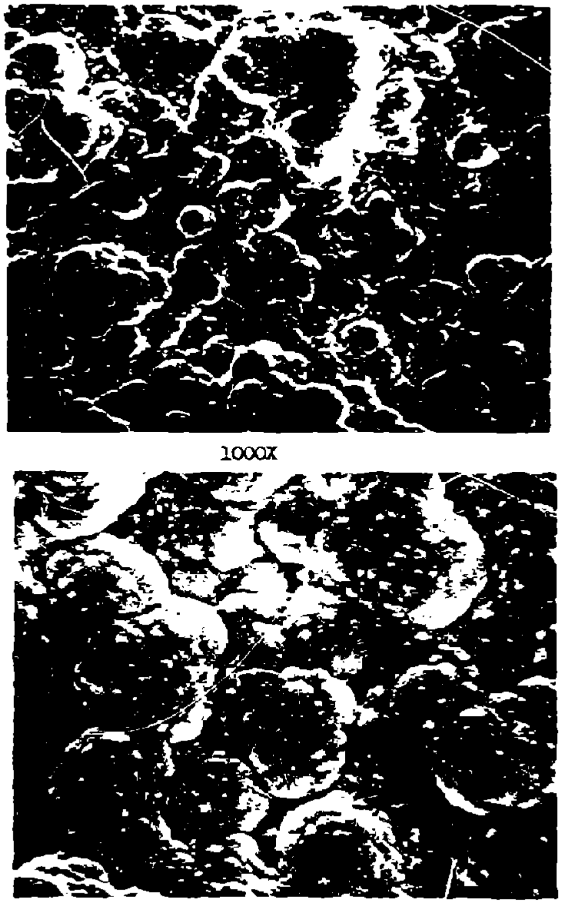


lightly etched



heavily etched

Figure 6. Cross Sections of 0.50-Mil Thick Electroplated Nickel Coatings (600X)



1000X

3000X

Figure 7. Surface Morphology of 0.50-Mil Thick Electroplated Nickel Coatings

TABLE IV

CORROSION OF NICKEL PLATED[1] URANIUM IN MOIST NITROGEN[2, 3]

Thickness of Plating (mm)	Thickness of Plating (mils)	Length of Test	Hydrogen Evolved (ppm)
No Plating		6 Weeks	180,000
0.013	0.5	8 Days	7,000
0.013	0.5	6 Weeks	35,000
0.025	1.0	6 Weeks	15
0.051	2.0	6 Weeks	10
0.076	3.0	7 Weeks	0
0.076	3.0	30 Weeks	0

[1] Specimens were plated in nickel sulfamate solution after etching in ferric chloride solution. Surface area of each specimen was approximately 3870 mm ($6\ in^2$).

[2] The nitrogen contained 2.8% H_2O, 97.2% N_2, temperature was 70°C. The specimens were sealed in glass tubes, evacuated for at least 3 hours under hard vacuum (<0.1 micron), backfilled with the desired gas mixture, sealed off and then placed in the oven for test.

[3] Data are from Johnson, Dini, and Zehr.[8]

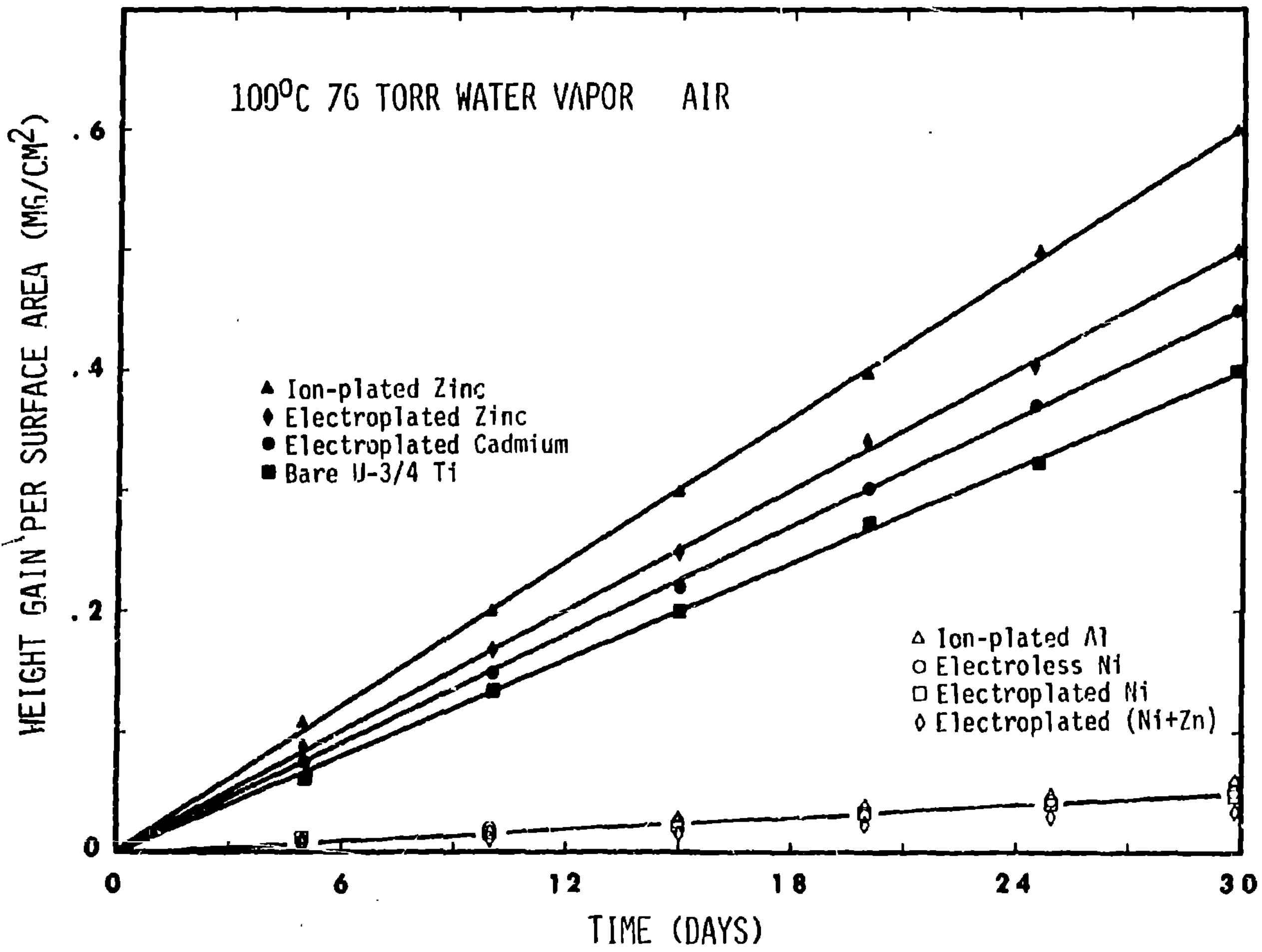


Figure 8. Relative Protection of U-3/4 Ti by Various Coating Materials in 10% R.H. Flowing Air at 100°C

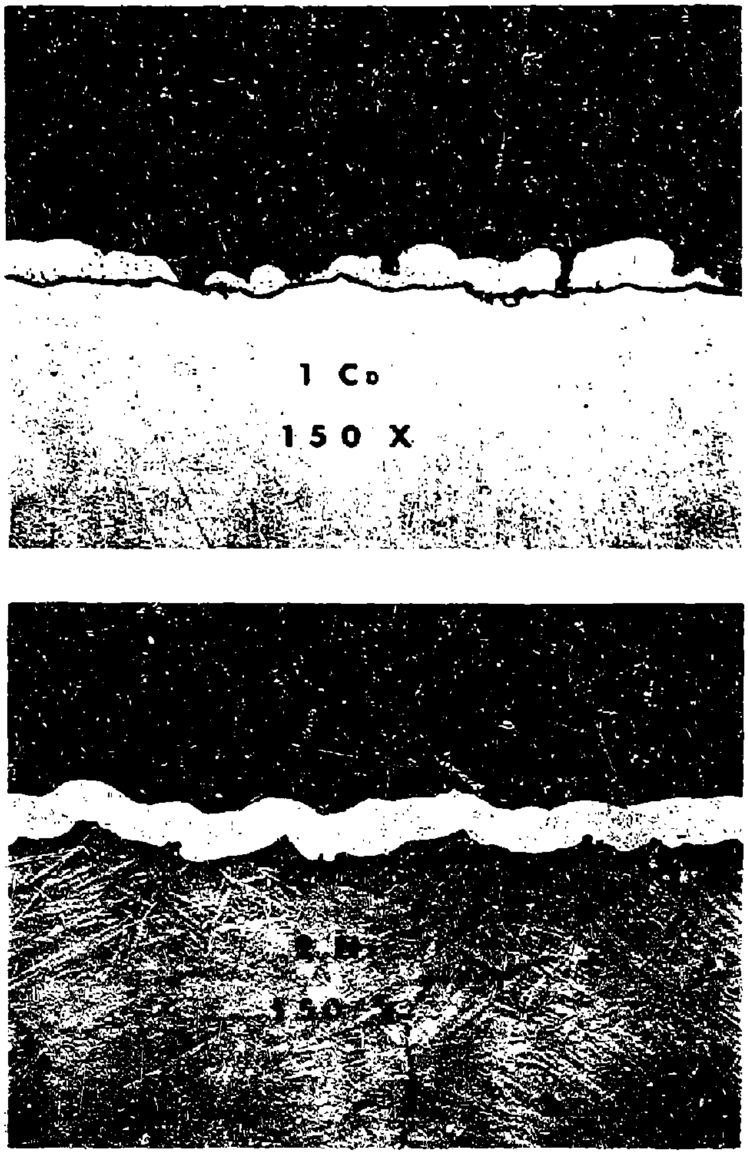


Figure 9. Metallographic Cross Sections of Cadmium-Plated and Nickel-Plated U-3/4 Ti Specimens

cadmium and zinc directly onto U-3/4 Ti does not result in an acceptable coating system.

In an aqueous chloride electrolyte, a coating may behave in either a protective, neutral, or destructive manner toward the substrate, depending on whether its electrochemical potential is negative, equivalent, or positive with respect to the substrate. The electromotive series for U-3/4 Ti and the various coating materials was determined in solutions of potassium chloride (KCl) at various concentrations (see Table V).[5] Two features can be extracted from this table. First, coatings of zinc and cadmium are electronegative to U-3/4 Ti and therefore should protect the alloy sacrificially. Second, aluminum and nickel are electropositive to U-3/4 Ti and thus the corrosion rate could be accelerated locally in the vicinity of any flaws in these coatings.

Uncoated and coated samples of U-3/4 Ti were suspended in a solution of KCl containing 50 parts per million (ppm) chloride ion (Cl^-) at room temperature for 30 days. The samples were intermittently removed from the solution, dried, and weighed. As shown in Figure 10, four important results were obtained from these tests. First, all coatings in the unflawed condition gave some protection to the U-3/4 Ti substrate. Second, when the electroplated nickel and ion-plated aluminum coatings began to fail, the corrosion rates, as shown by the slopes of the weight loss curves, accelerated until they became faster than that of bare material. Third, in spite of the poor adherence of the electroplated zinc and cadmium coatings and the ion-plated zinc coating, they imparted the predicted galvanic protection to the U-3/4 Ti. Fourth, the duplex coating with the zinc chromate finish provided the best long-term protection.

The reasons for the development and success of the duplex electroplated nickel plus zinc coating with a chromate finish are as follows. The electroplated nickel layer provides a good physical barrier to the corrosive environment. However, since nickel is noble with respect to the uranium alloy, corrosion is accelerated at any pinholes in the nickel plating. To overcome this limitation, zinc, which is sacrificial to the uranium alloy, is plated 0.2 mil thick over the nickel. Thus in a severe corrosion environment (i.e., salt water or salt fog), the zinc protects the uranium alloy at any holidays in the nickel layer. A zinc chromate finish is applied to protect the zinc during normal handling and storage conditions, thus extending the total lifetime of the uranium alloy part.

The value of this duplex coating was demonstrated in both the Air Force Materials Laboratory (AFML) GAU 8 uranium alloy penetrator program[10] and the Air Force - General Electric GAU 8/A Manufacturing Technology uranium alloy penetrator program.[11] In both of these programs, the 30-mm penetrator is made from the U-3/4 Ti alloy. Variations in the alloy's chemistry and in the manufacturing processes used, such as

TABLE V

ELECTROCHEMICAL POTENTIALS FOR U-3/4 Ti AND COATING MATERIALS[1]

KCl Molarity	10^{-2}	10^{-3}	10^{-4}	10^{-5}
PPM Cl^-	350	35	3.5	0.35
Metal	mV (SHE)	mV (SHE)	mV (SHE)	mV (SHE)
Zn	-795	-765	-735	-720
Cd	-465	-455	-450	-445
γ-Q	-450	-370	-345	-335
335-20	-445	-365	-325	-330
380-42	-450	-360	-325	-340
430-16	-450	-350	-330	-340
Al	-370	-310	-280	-280
Ni	+180	+190	+205	+200

Key: γ-Q - Water Quenched (W-Q)
335-20 - W-Q + Aged at 335°C for 20 hours
380-42 - W-Q + Aged at 380°C for 42 hours
430-16 - W-Q + Aged at 430°C for 16 hours
PPM - Parts per Million
SHE - Standard Hydrogen Electrode

[1] Data are from Weirick[5]

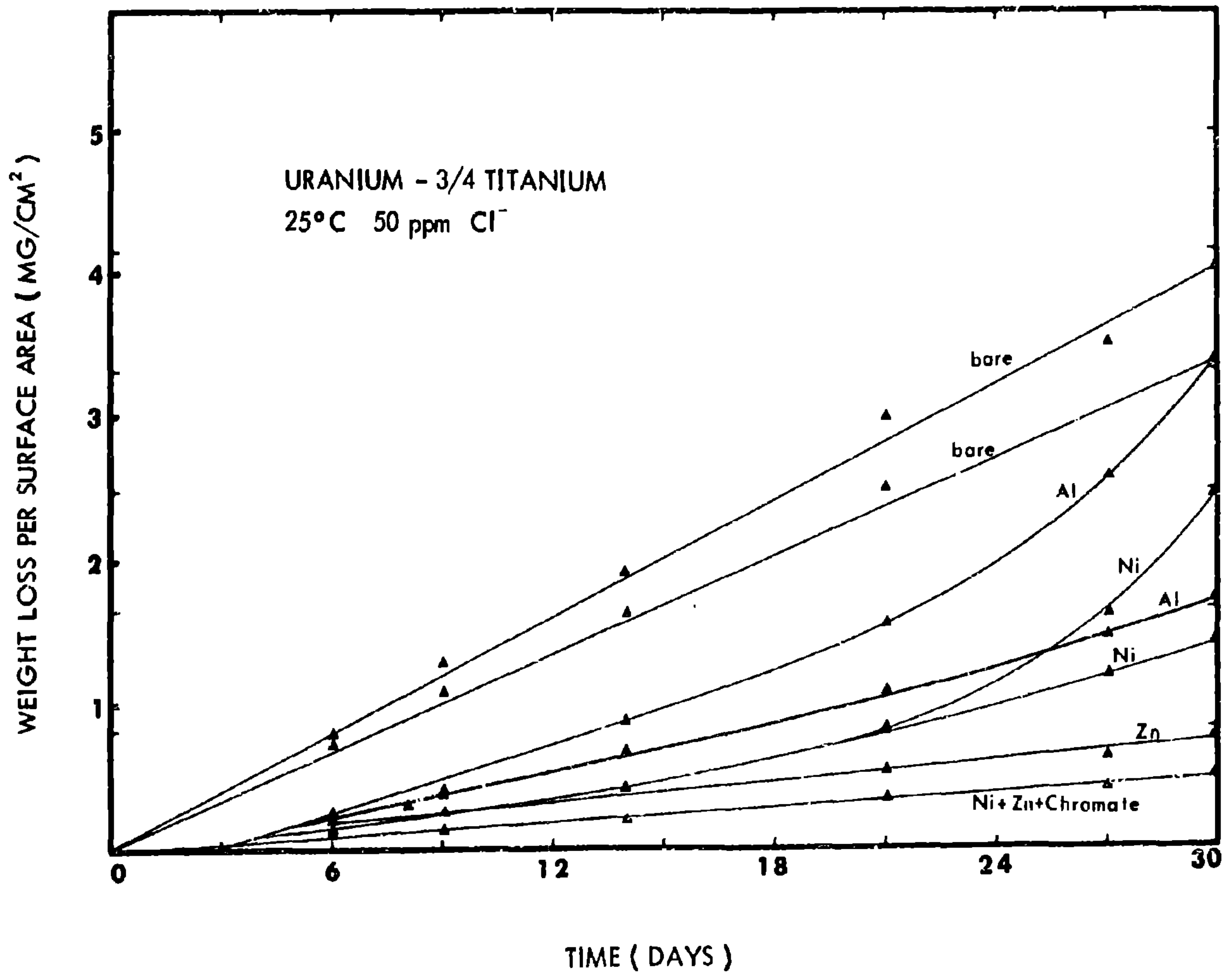


Figure 10. Relative Protection of U-3/4 Ti by Various Coating Materials in a Salt Solution Containing 50 ppm Cl$^-$ at 25°C

extrusion, swaging and forging, did not affect the application nor performance of the duplex coating. As shown in Figure 11, the coated penetrators lost weight in the salt fog environment because of the formation of nonadherent oxides and chloride complexes. The weight loss for uncoated penetrators that were tested was linear with time. As was expected, the overall corrosion rate for nickel-plated penetrators eventually surpassed the rate for the uncoated penetrators. The nickel-plated penetrators had very deep pits in areas where there was initial porosity in the coating. In fact, the pitting was so severe that, even though it was a localized reaction, it produced a larger weight loss and a more deleterious effect on the penetrator than the more uniform corrosion on the uncoated penetrator.

The penetrators which had been coated with the duplex coating had a remarkable resistance to the salt fog environment, as shown in Figure 11. Only after an extended test time, when the zinc chromate finish began to show evidence of failure, did the zinc begin to corrode; but not the U-3/4 Ti alloy.

Zinc Galvanizing

Galvanizing is the practice of coating iron or steel with a thin layer of zinc to protect the surface against corrosion. The most important galvanizing method is the hot-dip process, which consists of four steps: surface preparation, fluxing, immersing in molten zinc, and finishing. Surface preparation includes degreasing and pickling operations to remove oil, grease, and scale. The fluxing step is done immediately before immersing the part in molten zinc so that the flux removes any oxide that may have formed on the surfaces since cleaning. Finishing includes removing excess zinc by shaking, draining, or centrifuging; quenching (optional); chromating (optional); and inspection.

Very little information is available on the dip-coating of uranium with zinc. The British did some work in 1948,[12] and there followed some efforts in the United States in 1955.[13] The results agreed in that sound, adherent coatings were applied to the uranium parts by hot-dipping, and these coatings significantly improved the corrosion resistance of the parts. Chiotti et al.[13] noted that uranium forms only one compound with zinc, UZn_9. This compound was shown not to affect adversely the corrosion resistance of either zinc or uranium.

The value of zinc galvanizing in protecting U-3/4 Ti was demonstrated in the AFML GAU 8 penetrator program. Most penetrators galvanized for this program were done using the procedures described in Table VI. Further study indicated that steps 2-5 could be eliminated without affecting the quality of the coating. A galvanizing time of one minute was chosen to ensure that the surface of the part reached bath temperature and to allow

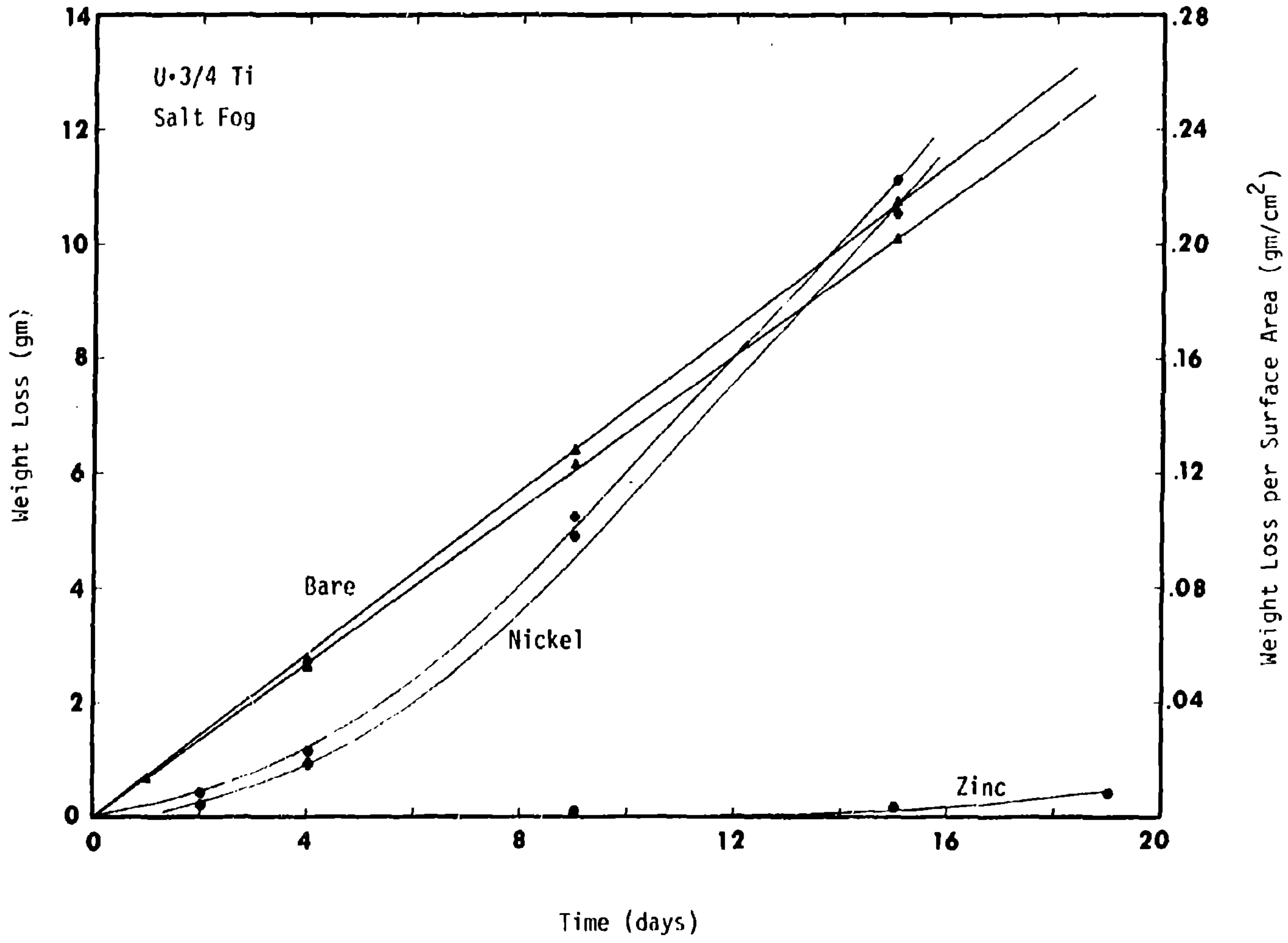


Figure 11. Corrosion and Relative Protection of U-3/4 Ti Penetrators in Salt Fog at 35°C

TABLE VI

GALVANIZING PROCEDURE

1. Vapor degrease in trichloroethylene.
2. Alkaline clean in Oakite 90* solution for ~5 minutes at 160-180°F.
3. Water rinse.
4. Pickle in 50 percent by volume solution HNO_3 to remove oxides.
5. Water rinse and dry.
6. Immerse part in flux consisting of 46.4 wt% KCl, 36.9 wt% LiCl and 16.7 wt% $ZnCl_2$ for two minutes at ~850°F. (It takes approximately 90 seconds for part to reach flux temperature.)
7. [†] Immerse part in molten zinc at 850°F for approximately 1 minute.
8. Immerse part in separate zinc pot which does not have flux on top for ~2 minutes at 850°F.
9. Remove excess zinc from part by shaking.
10. Air cool to room temperature.
11. Activate zinc surface by immersing in a 1 percent H_2SO_4 solution at ~120°F for 1-2 minutes.
12. Apply chromate coating by immersing in Granodine 90** solution for 10 seconds.
13. Water rinse and dry.

*Oakite Products Inc., Berkeley Hgts., NJ.

**Amchem Products, Inc., Ambler, PA.

[†] Steps 6 and 7 are done in the same pot by floating the flux on top of the molten zinc.

the formation of UZn_9 at the alloy surface. It was assumed that the diffusion process would provide a coating with better integrity than one created simply by having the zinc "freeze" on the surface. This is an assumption which has not been proven.

A single-dip process allowed some of the flux to adhere to the specimen and cause roughness. Dipping the parts a second time in a crucible containing only zinc caused all remaining flux to float to the surface, where it was skimmed before the part was removed. In an attempt to obtain smooth, uniform coatings, galvanized penetrators were initially quenched in either water or mineral oil. Another technique tried was to sprinkle ammonium chloride on the part as it was withdrawn from the galvanizing crucible. Very little benefit accrued from either of these efforts. A slow withdrawal from the zinc bath appeared to produce the smoothest, most uniform coating.

All galvanized penetrators were given a chromate conversion coating to further enhance corrosion resistance. The chromating was done by immersion in a proprietary solution, Granodine 90 (Am-Chem Products, Ambler, Pa.). When zinc-coated parts are immersed in chromating solutions, an amorphous chromate film, typically less than 0.02 mil thick, is precipitated on the surface.

The protectiveness afforded to the U-3/4 Ti alloy by galvanized zinc in a hot, moist nitrogen atmosphere is shown in Figure 12. The weight gain curve for the alloy in an uncoated state shows that the corrosion rate was very rapid for the first few days and then changed to a fairly constant, but much slower, rate. This dramatic change was partly due to the onset of spallation in the outer layers of uranium dioxide. In fact, the magnitude of this spallation was great enough to produce an overall weight loss of oxide from the penetrator. Figure 12 also shows that electroplated nickel and galvanized zinc protected the penetrators from any significant corrosion in the hot, moist nitrogen environment. The weight gains shown for the zinc galvanized penetrators were due to the formation of a white, zinc oxide tarnish film and not to any degradation of the uranium alloy.

The corrosion data generated from salt fog tests for uncoated and coated penetrators has already been shown in Figure 11. The curve labeled "zinc," which was previously discussed as pertaining to the duplex electroplated nickel plus zinc coating, also applies to the zinc galvanized coating. Again, the data show that after an extended time period, the zinc began to corrode, but not the uranium alloy.

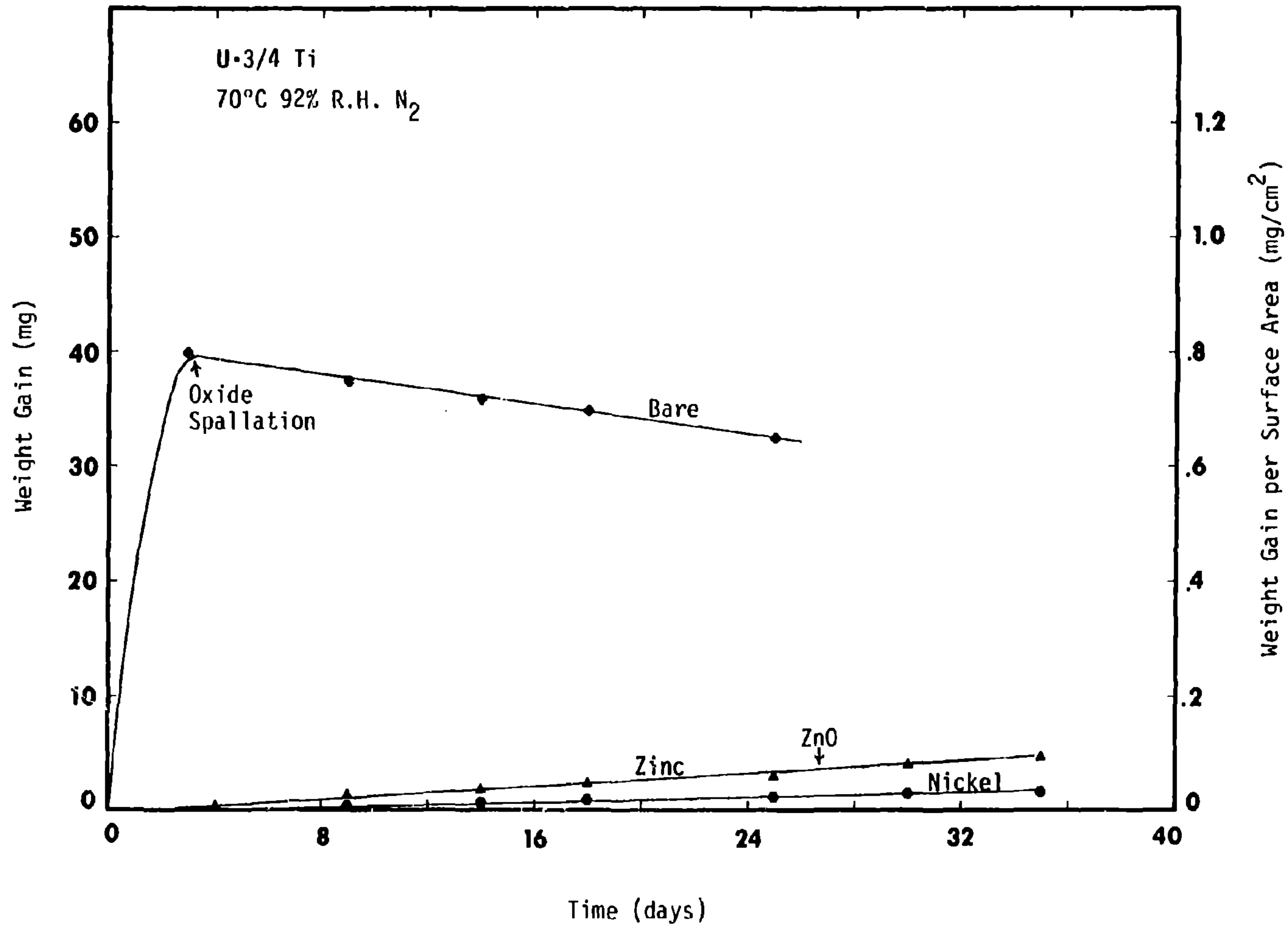


Figure 12. Corrosion and Relative Protection of U-3/4 Ti Penetrators in 92 Percent R.H. Nitrogen at 70°C

Present Development

Electrodeposited Zinc-Nickel

A technique developed by Dini and Johnson[9] for electroplating a zinc rich alloy of zinc-nickel on uranium looks very promising. This alloy has a composition of approximately 90 percent zinc and 10 percent nickel by weight as determined by wet chemical analysis. The etching and plating techniques and solutions as outlined in Table III for nickel were used for plating this alloy with the exception that a 90 zinc-10 nickel sulfamate plating bath was used instead of the pure nickel sulfamate one. Interestingly, the uranium alloy substrate accepts the zinc-nickel alloy as if it were pure nickel, not containing any zinc. The deposit appears to be very adherent, uniform and relatively pinhole free.

There are two major advantages of this coating over the duplex coating of electroplated nickel plus zinc. First, the zinc-nickel alloy coating can be applied in one step instead of two, and thus both time and cost can be reduced and plating tolerances can be tightened. Second, the cost per pound for zinc is five times lower than for nickel and thus, for a given total plating thickness, the zinc-nickel alloy coating is significantly less expensive than the duplex coating.

An acceptable zinc chromating solution must be developed for this zinc-nickel alloy electrodeposit because the commonly used chromating solutions do not give a proper chromate film when applied to this alloy. In spite of this drawback, preliminary corrosion tests on both steel panels and uranium alloy coupons coated with this zinc-nickel alloy show that the coating offers good protection from a salt fog atmosphere.

Hot-Dipped Tin-Zinc

One significant limitation on the use of galvanized zinc is the lack of tolerance control on coating thickness. One solution to this problem is to alloy the zinc with a lower temperature eutectic former such as tin. The zinc-tin eutectic is at 198°C, and thus zinc-tin coating could be further processed using hot air devices to smooth and thin the coating.

A study is in progress which includes an investigation of the electrochemistry of the Sn-Zn alloy system with respect to the U-3/4 Ti alloy and also includes the generation of corrosion data on the sacrificial protection of the uranium alloy by Sn-Zn galvanized coatings. Figure 13 shows the Sn-Zn binary phase diagram, which is classified as a simple eutectic. The most desirable composition for a coating to be subsequently hot worked after application would be the alloy with the lowest melting point, i.e.,

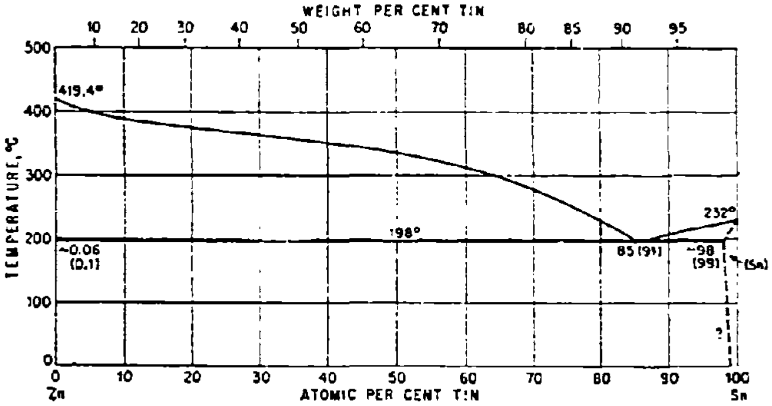


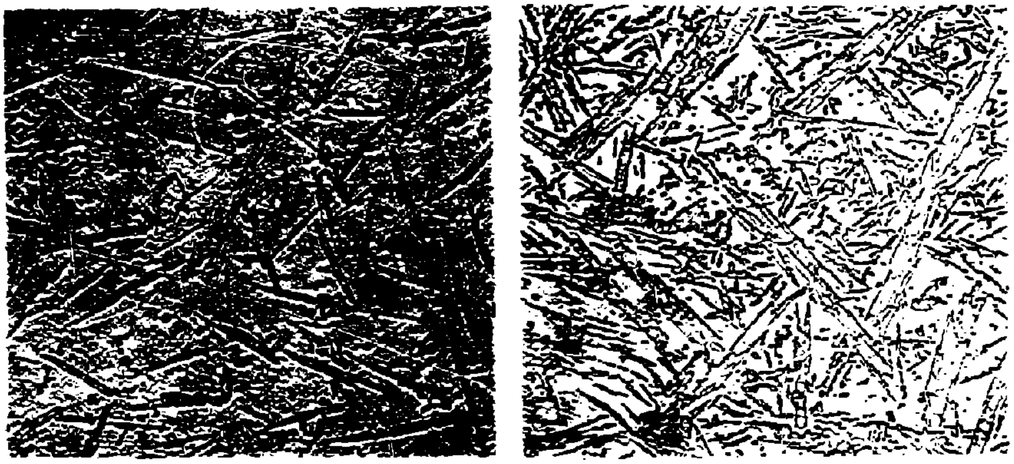
Figure 13. Zinc-Tin Phase Diagram

near the eutectic composition of 89 Sn - 11 Zn by weight. From the phase diagram, it is expected that any alloy with a composition rich in zinc compared to the eutectic composition would consist of the eutectic phase plus free zinc. This free zinc should provide the desired sacrificial protection.

Alloys of Sn-Zn were made at ten percent increments by weight over the entire alloy range (see Figure 14). As expected, the phases are a mixture of the eutectic phase plus free zinc (identification made by electron microprobe analysis). The amount of eutectic and free zinc follows the binary lever rule very accurately. The corrosion potential of each of these alloy compositions was measured in a 10^{-2} Molar potassium chloride solution (see Figure 15). This figure also identifies the U-3/4 Ti corrosion potential in this electrolyte. All of the compositions measured exhibited a corrosion potential more electronegative, or sacrificial, with respect to the uranium alloy. Thus any of these compositions could be used as a replacement for the pure zinc coating.

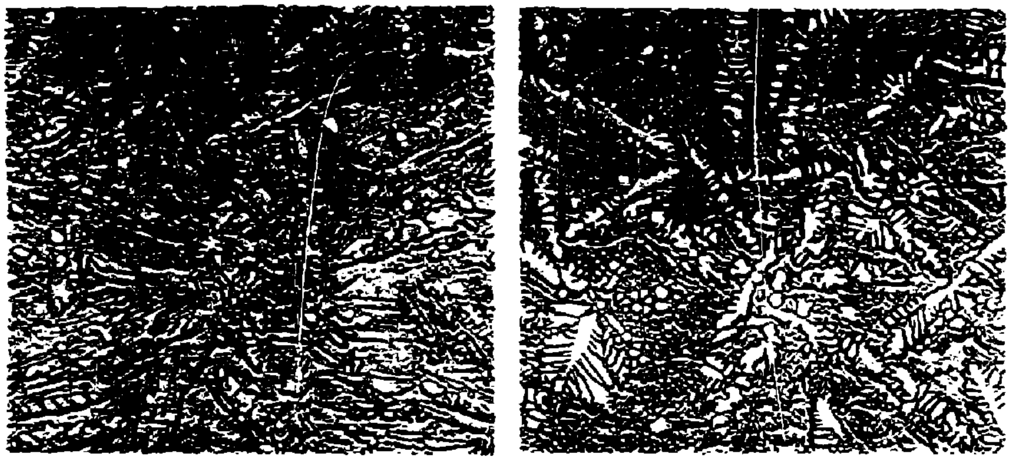
Two kinetic measurements were made to verify the thermodynamic predictions obtained from the corrosion potential measurements. In the first type of test, electrical couples of coating material and U-3/4 Ti were tested in a KCl electrolyte. The arrangement of the couple and associated monitoring equipment are shown schematically in Figure 16. Upon submersion of the couple into the electrolyte, a flow of metal ions into solution is accompanied by a movement of electrons through the electrical circuit. The magnitude and direction of this electron flow or corrosion current are recorded as functions of time. The results indicated that all of the tin-zinc alloys produced a negative corrosion current, i.e., they corroded sacrificially and protected the U-3/4 Ti. In addition, no corrosion products formed on the Sn-Zn alloys during the tests which could have passivated them.

In the second type of test, samples of U-3/4 Ti were coated with the Sn-Zn alloys by the hot-dipping process and then subjected to a corrosion test in salt fog. Before the corrosion test, each of the coatings had ten holes of 5 mils diameter drilled through the coating to the U-3/4 Ti substrate to simulate holidays in the coating which may arise due to processing or handling. If the coating is then truly protective, it will sacrifically protect the alloy at these pores. As predicted, the results from these corrosion tests indicated that all of the compositions tested do protect the uranium alloy sacrifically. Work is thus progressing on developing and qualifying the alloy coating with an 80 Sn - 20 Zn composition, that composition closest to the eutectic composition but still containing an appreciable amount of free zinc. This development must include the formulation of a chromating solution that will adequately chromate this tin-rich alloy.



20Zn - 80Sn

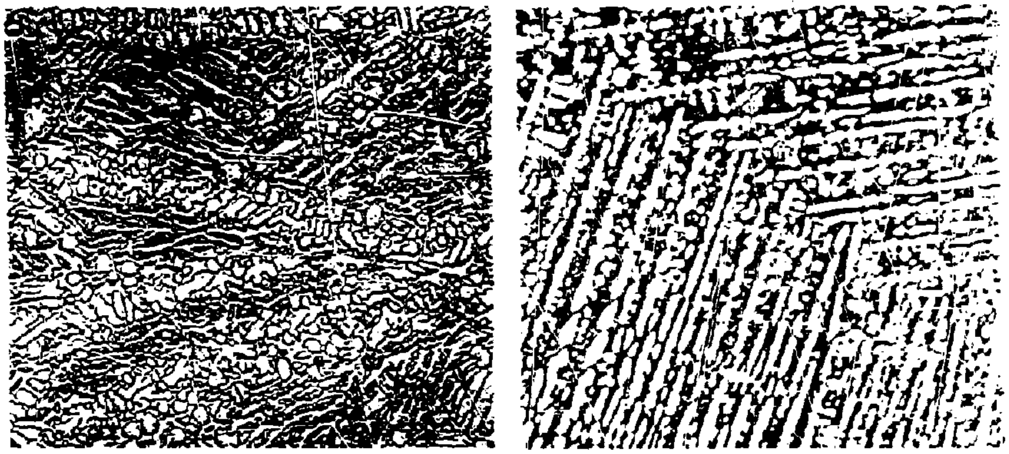
30Zn - 70Sn



40Zn - 60Sn

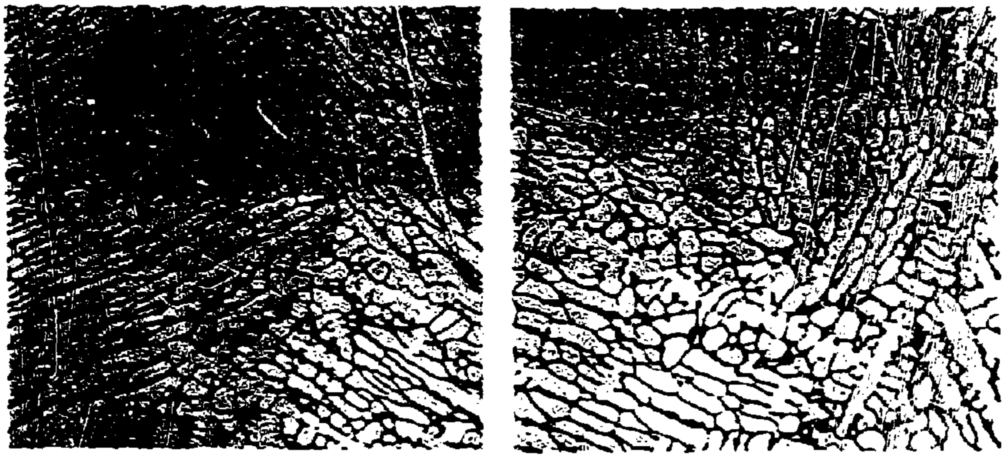
50Zn - 50Sn

Figure 14. Microstructure of Zinc-Tin Alloys



60Zn - 40Sn

70Zn - 30Sn



80Zn - 20Sn

90Zn - 10Sn

Figure 14. (continued)

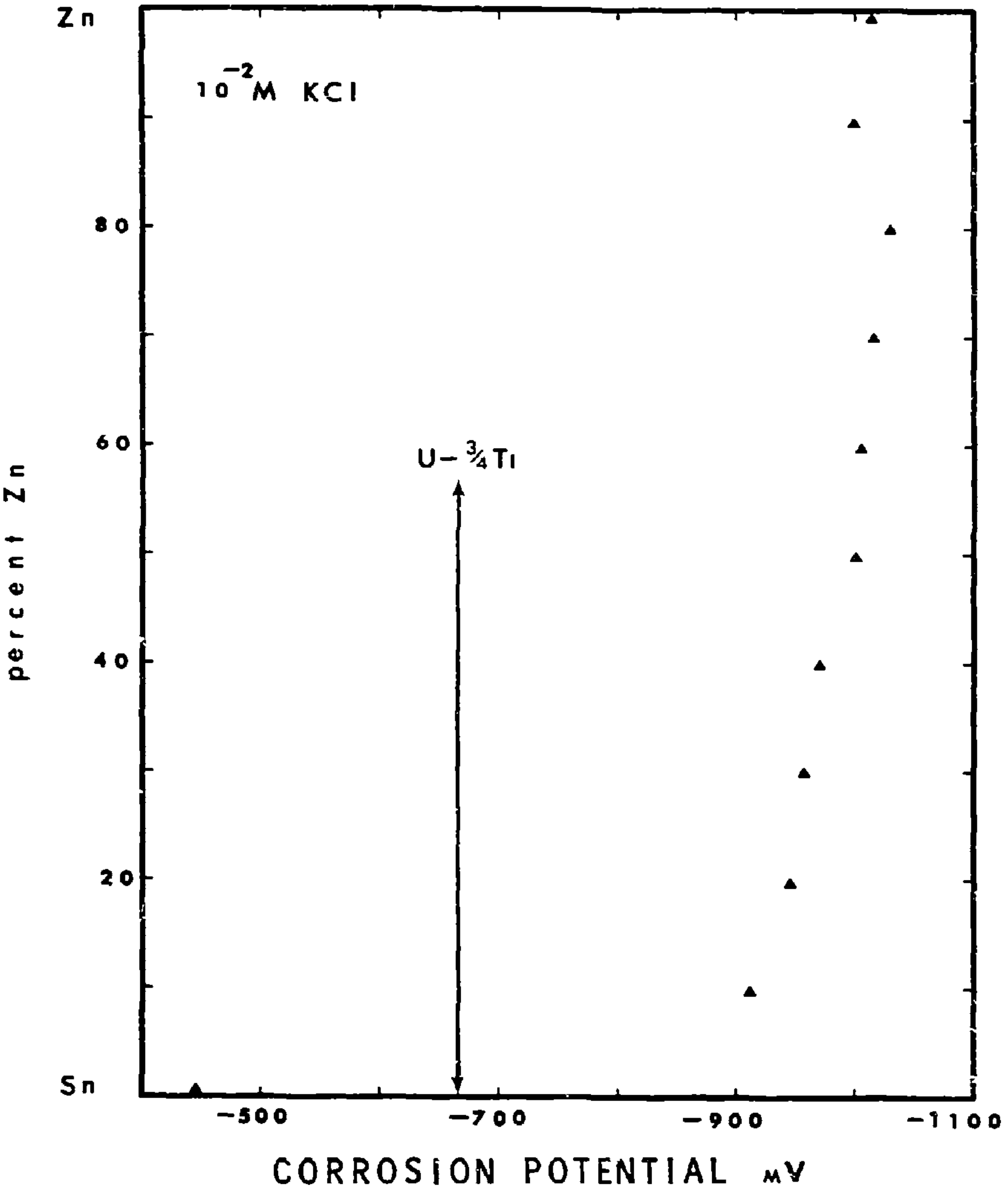


Figure 15. Corrosion Potential of Zinc-Tin Alloys in 10^{-2}M KCl

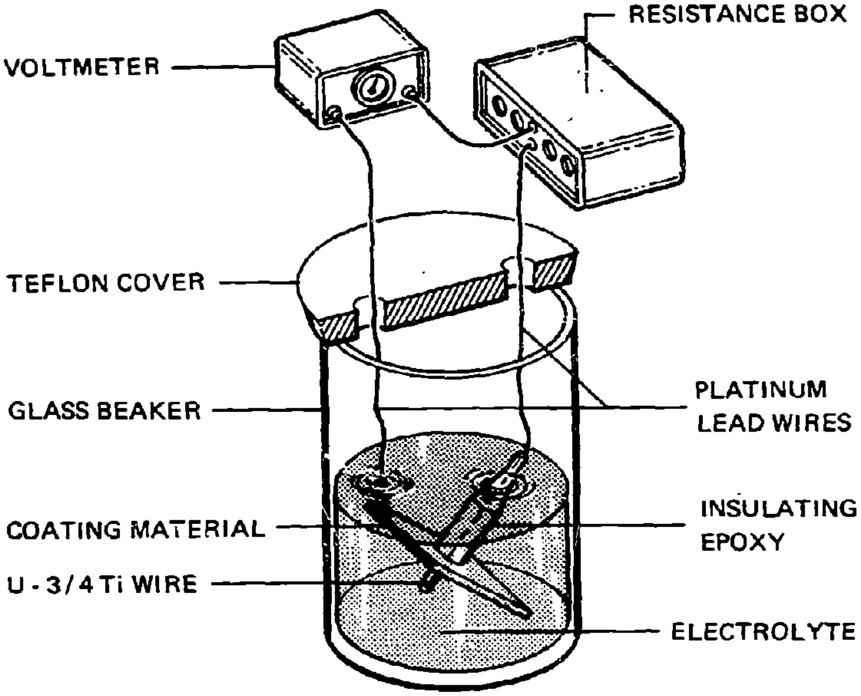


Figure 16. Schematic of U-3/4 Ti - Coating Material Galvanic Couple With Associated Monitoring Equipment

Conclusions

Presently, a paint coating on uranium and uranium alloys will only provide short term protection in non-aggressive environments. In environments which have a significant moisture content, and particularly if oxygen depletion is also possible, an organic film on uranium and uranium alloys can act in a deleterious, rather than protective, manner. Even in low-moisture content, non-aggressive environments with appreciable oxygen availability, water will eventually permeate the coating, react with the metal substrate, and detach the paint coating.

The metallic coatings which have demonstrated the most protectiveness of uranium and uranium alloys are based on either an electrodeposited nickel or galvanized zinc system. Electrodeposited nickel alone is an adequate coating in a non-condensing environment. However, because nickel is more noble than uranium and uranium alloys, an electrolyte film on the coating can accelerate the corrosion reaction at holidays in the coating such that the corrosion rate of the uranium or uranium alloy can actually surpass the rate measured for uncoated material. This deficiency in the electrodeposited nickel coating has been corrected by either electrodepositing a sacrificially-protective layer of zinc on top of the nickel or co-depositing the zinc with the nickel in a zinc-rich mixture. Both of these combination coatings have proven to be very good for corrosion protection in the most aggressive of environments. The one remaining drawback of electrodeposited coatings is their expense. The number of steps required for proper surface preparation before plating as well as the time taken to do the plating results in a significant labor expense. In addition, nickel is expensive.

The biggest advantage of galvanized zinc coatings is their low cost. Tests done on galvanized penetrators have demonstrated that protective coatings were obtained after only a degreasing operation prior to the fluxing soak and hot dip. The only additive cost is the subsequent finishing step necessary to remove excess zinc and smooth the coating. The degree of complication of this finishing step is dependent upon the tolerance and finish requirements demanded by the particular application. In conclusion, the most effective coating from the standpoint of corrosion protection and cost is a galvanized zinc or tin-zinc alloy.

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