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Corrosion Resistance of Zinc-Nickel Plated U-0.75 Ti

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CORROSION RESISTANCE OF ZINC-NICKEL PLATED U-0.75 Ti*

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ABSTRACT

As part of a program for the U. S. Army directed at improving the corrosion performance of U-0.75 Ti, specimens were coated with Zn-10 Ni alloy electroplate and then subjected to various corrosion tests. This work revealed that the Zn-Ni coatings provided good protection for U-0.75 Ti in salt fog and in non-sealed moist-nitrogen systems. In sealed, moist-nitrogen environments the Zn-Ni coatings deteriorated quickly and provided no protection. Some plating with Zn alone, using some of the new non-cyanide plating solutions, was also attempted, but the results were inconsistent.

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Introduction

The U. S. Army, Picatinny Arsenal, is developing a new generation of antitank munition that utilizes the SLL depleted-uranium alloy U-0.75 Ti. U-0.75 Ti is considered a lean uranium alloy, and is susceptible to corrosion in certain environments. A protective coating may be necessary to allow long-term storage.

A preliminary corrosion and coating study was completed for the Army in 1976.^{1,2} The work described in this report is a continuation of the coatings development studies.

The objective of this work was for economic considerations to replace with a single coating the established duplex coating of nickel and zinc which previously had been shown to successfully protect U-0.75 Ti from corrosion.³ Two approaches were considered: deposition of pure zinc coatings and deposition of zinc-nickel alloy coatings. Although past efforts have resulted in very little success with deposition of pure zinc on uranium from a conventional cyanide solution, a number of non-cyanide zinc plating solutions have been developed in recent years.⁴ Hence it was deemed worthwhile to evaluate some of these for plating on uranium. Alloy coatings of zinc-nickel were included since work by ourselves and others revealed that over steel this type of deposit is superior to pure zinc.^{5,6} The zinc-nickel coatings also proved to be far superior for protecting uranium than electroplated zinc coatings. Thus the main emphasis of this report is on the Zn-Ni results, and only a limited discussion of the zinc electroplating work is given in the last section.

Zinc-Nickel Plating Details

The formulation for the zinc-nickel plating solution used for this work is shown in Table 1. Details on operation of this solution and influence of plating variables such as current density and temperature on deposit appearance, composition, and efficiency are found in Reference 5. The solution is basically Roehl's⁶ with some changes. He used the chloride salts of zinc and nickel whereas we used zinc sulfate and nickel sulfamate. The reason for this change

TABLE I

ZINC-NICKEL SOLUTION FORMULATION

Zinc Sulfate ($ZnSO_4 \cdot 7H_2O$)	266 g/l
Zinc	60 g/l
Nickel Sulfamate*	190 ml/l
Nickel	34 g/l
Sodium Lauryl Sulfate	0.375 g/l
Surface Tension	35-40 dynes/cm
pH	5.0

*Nick 24 sulfamate nickel concentrate, Allied-Kelite Products, Div., the
Hercules Co., Des Plaines, Ill.

The susceptibility of uranium and its alloys to attack by chlorides. Roehl⁶ recommended a small amount of acetic acid as a buffer to promote ease of pH control. We found this to be unnecessary, and furthermore discovered (as a result of some Huitl cell tests) that acetic acid reduced the covering power of the solution. A wetting agent (sodium lauryl sulfate) was used to lower the surface tension of the solution to eliminate pitting. Zinc anodes were used for most of the work, but alloy anodes of the approximate composition Zn-10 Ni would probably be quite suitable since the composition of the deposit is ~5-10% Ni with the balance Zn.

Corrosion Tests

Experimental Procedures -- Most of the specimens were etched in 1400 g/l ferric chloride solution, plated with varying thicknesses of zinc-nickel at 214 A/m² (20 asf), and then given a chromate treatment by immersion in Chromidine 90* for 10 seconds. A few specimens were left for testing in the unprotected state. Three kinds of environments were used for corrosion testing:

1. Salt fog environment as specified in Mil-Std 810B, Method 509. Briefly described, this consists of a salt fog which contains 5 wt.% NaCl in atomized water which is continually flushed through the chamber while being maintained at 35°C. Thus specimens are continuously exposed to a thin film of fresh, aerated salt water.

*Product of AMCHEM Products, Inc., AMBLER, PA.

2. Deoxygenated nitrogen maintained at 70°C and containing 95% relative humidity (RH). Specimens were allowed to "breathe" in this test, i.e., any created hydrogen as was allowed to vent to air and it was possible for oxygen to enter the test environment.
3. Moist nitrogen maintained at 74°C in sealed glass ampoules. This environment was made by transferring water from a weighed quantity of barium chloride dihydrate to glass ampoules, adding nitrogen, and placing the ampoules in an oven at 74°C. At this temperature, the atmosphere inside the ampoules was saturated. The ampoules had side arms with break seals for extracting gas samples for analysis so that hydrogen generated during the test could be measured.

Two tests were made in the salt fog environment, each with coupons of different size. For one test the specimens were 1.3 x 2.5 x 0.5 cm (0.5 x 1.0 x 0.2 in.), and for the other they were 2.5 x 7.5 x 0.64 cm. For test environment 2, U-0.75 Ti coupons approximately 1.3 x 2.5 x 0.5 cm were used; for environment 3, the U-0.75 Ti tensile specimens were 0.63 cm (0.25 inch) in diameter with a 2.5 cm (1 in.) gauge length (per ASTM E8-69, 1972, Fig. 8 therein, and Federal Standard 151).

Evaluation procedures for determining test results included both visual observation and gravimetric methods. Photographs of specimens were taken after the tests for visual documentation. Plots of change in weight as a function of time for each specimen were made to determine relative corrosion rates. Specimens removed from the vented nitrogen environment (2) were weighed as removed, while those tested in salt fog were rinsed before they were weighed in order to remove loose, porous corrosion products. Specimens from the sealed ampoules (3) were tensile tested in vacuum at 10^{-6} Torr at 22°C. Crosshead speed was 1.3 mm/min (0.050 in./min). The specimens were then sectioned for hydrogen analysis by the Powell¹⁷ method. This consists of mass spectrographic determination of the instantaneous rate at which hydrogen is thermally evolved from a sample, thus allowing the hydrogen produced by the decomposition of surface contamination to be distinguished from the hydrogen evolved from the sample.

Results

Salt Fog -- Figures 1-3 summarize the corrosion data generated for this environment. The specimens lost weight because of the formation of non-adherent oxides and chloride complexes.³ The weight loss was fairly constant with time. The weight loss for a specimen plated with only 1 μm of zinc-nickel was greater than that of the bare material. Of interest is the fact that the slope of the curve for the thinly plated (1 μm) specimen was the same after 5 days in salt fog as that for bare U-0.75 Ti. This plated specimen had very deep pits in areas where there was initial porosity in the coating. Specimens with thicker zinc-nickel coatings showed increasing resistance to salt fog environment as a function of thickness. A 4.8- μm coating protected the U-0.75 Ti for 13 days before the slope of the weight loss curve changed to that for bare U-0.75 Ti. Coatings of 15 to 30 μm provided excellent corrosion protection. Results with the 30 μm thick Zn-Ni deposits closely parallel earlier work with a duplex coating of nickel plus zinc (also shown in Fig. 1.)

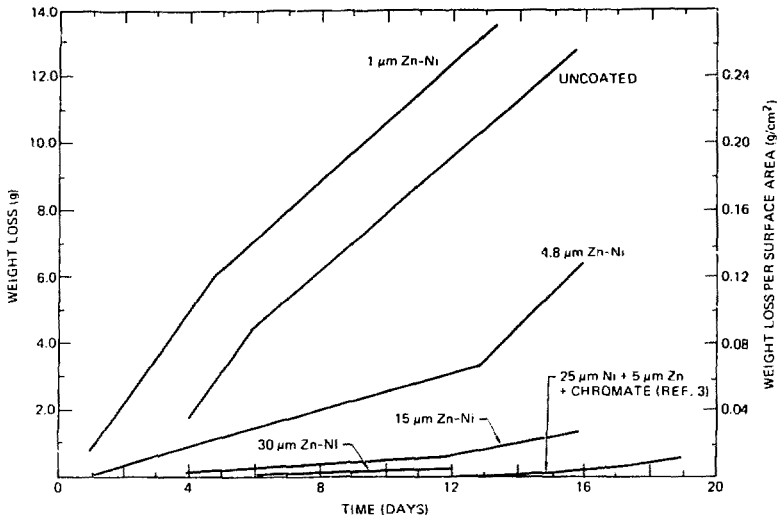


Figure 1. Salt Fog Results for Bare and Zn-Ni Plated U-0.75 Ti

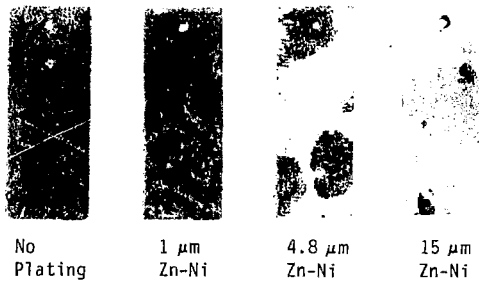


Figure 2. Specimens After 16 Days of Salt Fog (Specimen Size: 2.5 x 7.5 x 0.64 cm)

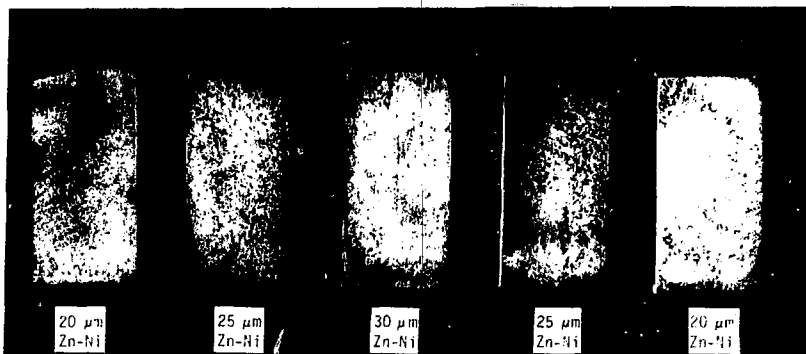


Figure 3. Specimens After 12 Days of Salt Fog
(Specimen Size: 1.3 x 2.5 x 0.5 cm)

Of additional importance is the fact that the chromate coating on the specimens included in these tests was very thin and colorless. Use of an olive drab finish -- a much heavier coating -- would probably lead to increased protection, as it does with pure zinc coatings.

Vented Moist Nitrogen -- Six U-0.75 Ti specimens, plated with a nominal 25 μm (1 mil) of zinc-nickel, were exposed to this environment for 27 days. The weight loss versus time curve for these specimens is shown in Figure 4 along with data for uncoated U-0.75 Ti. The protective feature of the zinc-nickel deposit is quite evident when the data for coated and uncoated samples are compared. Although there was some scatter in the data for the plated samples, all were noticeably more resistant to corrosion than unprotected samples. Figure 5 shows the specimens after completion of the test; no corrosion or degradation is evident.

Unvented Moist Nitrogen -- The data from this test were not as encouraging as those from the other two tests. Noticeable degradation was seen within 4 weeks of exposure. On many areas of each sample the coating exfoliated, as shown in Figure 6. Hydrogen generated during the test was very high for all four specimens, > 120,000 ppm (Table II). Tensile test data, also shown in Table II, revealed that the specimens coated with Zn-Ni suffered a loss in ductility properties as a result of exposure in the sealed ampoules.

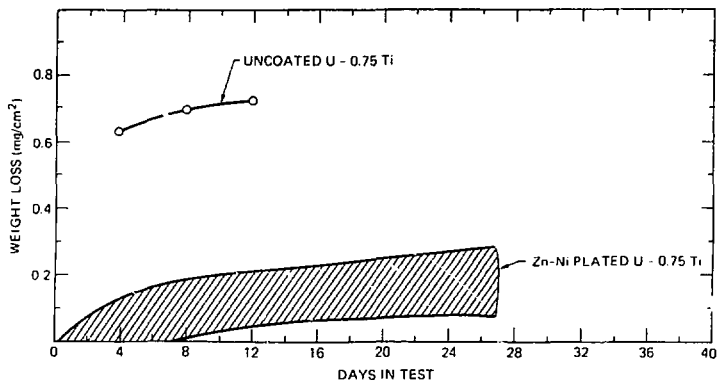


Figure 4. Moist Nitrogen Results for Bare and Zn-Ni Plated U-0.75 Ti



Figure 5. Zn-Ni Plated U-0.75 Ti Samples After 27 Days Exposure to Moist Nitrogen

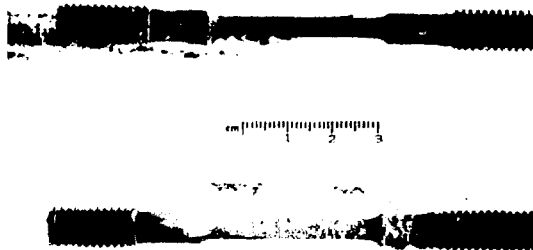


Figure 6. Zn-Ni Plated U-0.75 Ti Samples After 4 Weeks Exposure to Moist Nitrogen at 74°C in a Sealed Container

Table II

DATA FOR ZINC-NICKEL PLATED U-0.75 Ti AFTER EXPOSURE TO MOIST NITROGEN IN SEALED AMPOULES

Zn-Ni Plating Thickness (μm)	Length of Test ^a (weeks)	Hydrogen Evolved (ppm)	Ultimate Strength ^b (MN/m)	Elongation ^c (%)	Reduction in area (%)
None-Control	10	224,000	1420	11.3	8.0
14	10	144,000	1305	10.5	7.4
27	10	160,000	1425	3.7	3.7
11	30	130,000	1370	4.3	5.2
22	30	120,000	1400	4.3	2.0

^aThe atmosphere was water saturated moist nitrogen at 74°C.

^bTested at a strain rate of 0.001 sec⁻¹.

^cIn 25.4 mm (1 in.).

Zinc Plating

Chloride, sulfamate, and pyrophosphate solutions were evaluated as potential candidates for deposition of zinc alone on U-0.75 Ti. Solution details are given in Table III. Results with all three were sporadic: On some occasions, sound deposits were obtained, but on others the deposits did not fully cover the substrate or the coatings blistered. These deficiencies, coupled with the generally favorable results obtained with Zn-Ni coatings, led to abandonment of work on zinc deposits.

Table III

ZINC PLATING SOLUTION FORMULATIONS

<u>Chloride</u>	
Zinc Chloride	31.5 g/l
Ammonium Chloride	360 g/l
Du-Zinc Cl-H4 ^a	As recommended by supplier
Du-Zinc Cl-L3 ^a	As recommended by supplier
Temperature	25°C

<u>Sulfamate</u>	
Zinc Sulfamate	250 g/l
pH	2.0 - 4.0
Temperature	49 - 60°C

<u>Pyrophosphate</u>	
Zinc Pyrophosphate	60 g/l
Potassium Pyrophosphate	300 g/l
P ₂ O ₅ /Zn	12/1
Temperature	38°C

^aDu-Tone Chemical Co., Inc., Waukegan, Ill.

Summary

This work shows that an electrodeposited Zn-Ni alloy coating offers promise for protecting U-0.75 Ti from corrosion. Excellent protection was obtained in salt fog environment with coatings as thin as 15 μm . Similarly, good protection was obtained in a moist nitrogen test wherein the specimens were allowed to "breathe" (i.e., the container was not sealed). When the moist nitrogen test was performed in a sealed container, severe degradation was obtained. Exfoliation of the plating was noted, as well as some reduction in ductility properties.

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