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Adhesion of Electrodeposited Coatings on U-Ti and Mulberry

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ADHESION OF ELECTRODEPOSITED COATINGS ON U-Ti AND MULBERRY

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ABSTRACT

Quantitative test data are presented for two etched and plated uranium alloys, U-0.75 Ti and mulberry (U-7.5 Nb, 2.5 Zr). Conical head tensile tests showed that the bond between nickel plating and U-Ti was stronger than that between nickel plating and mulberry. Ring shear tests showed that electroplated nickel coatings are more adherent than other coatings applied to U-Ti. Utilizing a newly developed etchant for mulberry, large cylinders of this material were joined to aluminum and then tensile tested. Results showed that the strength of the joint was directly influenced by the taper angle on the mulberry.

INTRODUCTION

Uranium is one of the more difficult metals to plate upon because its surface has a tendency to become passive. If the proper procedures are used, however, it is possible to obtain suitable mechanical adhesion between uranium and electrodeposited coatings (1). The most successful techniques involve chemical or electrolytic treatment of the uranium in acid solutions containing chloride ions, followed by removal of the chloride reaction products in nitric acid before plating (2,3). These treatments do nothing more than provide a much increased surface area with many sites for mechanical interlocking or "interfingering" of the deposit; however, extremely good adherence can be obtained.

The above comment regarding passivity is even more applicable with uranium alloys which are a breed of materials containing various alloying elements for improving the corrosion resistance and tensile properties. As a rule of thumb, the higher the alloy content, the harder it is to etch the alloy satisfactorily for plating. This is not to say that techniques have not been developed for plating on various alloys of uranium. Earlier work provided procedures and data on the plating of U-Ti, U-Nb (3), and QUAD (4). This work, including data for U-0.75 Ti and mulberry, is a continuation of some of the earlier effort

METALLURGICAL HISTORY OF U-Ti AND MULBERRY

The U-0.75 Ti alloy used in this work was solution heat treated for 4 hours at 800C in vacuum and water quenched. The material was then aged at 380C for 6 hours in argon and water quenched.

The mulberry alloy was solution heat treated for 4 hours at 800C in vacuum and water quenched. The material was then aged at 150C for 1 hour and water quenched.

ADHESION TESTS

Two different kinds of tests, ring shear and conical heat tensile, were used to provide quantitative data on the adhesion of coatings to the uranium alloys. To prepare ring shear specimens, a cylindrical rod is coated with separate rings of plating of predetermined width. The rod is then forced through a hardened steel die having a hole larger in diameter than the rod but less than that of the rod plus coating. The area of the test specimen and the load required to cause failure are used to calculate strength. Specimen dimensions are shown in Fig. 1. Other details on sample preparation and test procedures have been described elsewhere (5).

With the conical head tensile tests, the electrodeposit, the substrate, and the bond between the two are tested in a tensile fashion, the bond being normal to the loading direction. Flat panels are plated on both sides with thick electrodeposit. Conical head specimens are machined per Fig. 2 and then tested using standard tensile testing procedures. As with the ring shear tests, additional details on sample preparation and testing are available in Reference 5.

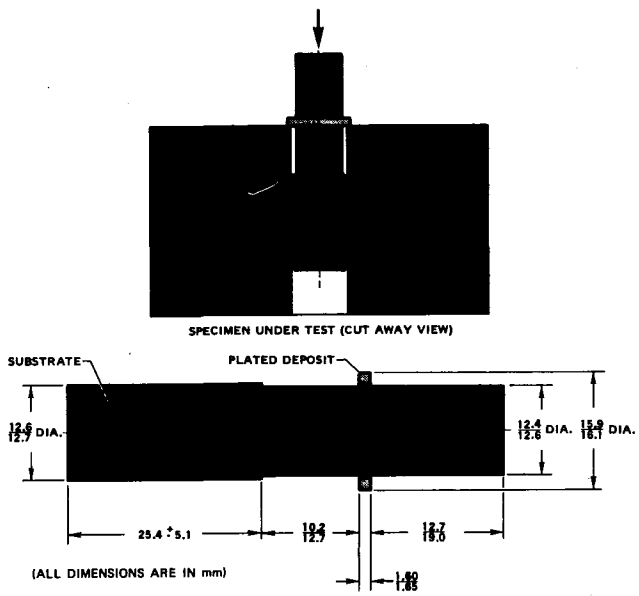

Fig. 1. Ring Shear Test Specimen and Die

RING SHEAR TESTS U-Ti

Earlier work in the literature contains information on etched and nickel plated U-Ti (3). Noticeably lacking from the literature, however, are data for uranium or uranium alloys plated with deposits other than nickel. Recently, some work was done at Sandia wherein copper and electroless nickel were plated on U-0.75 Ti to obtain this kind of information. All specimens were etched in ferric chloride solution prior to plating. Data are presented in Table I along with comparable data for nickel plated U-Ti. This information very clearly shows that the bond between U-Ti and copper or electroless nickel is considerably inferior to that between U-Ti and nickel. The reasons for the superiority of nickel over copper or electroless nickel are not known. However, this result is consistent with observations made at Sandia with unalloyed plated uranium during the past 12 years. Nickel has consistently been superior to all other deposits in adhering to uranium and its alloys.

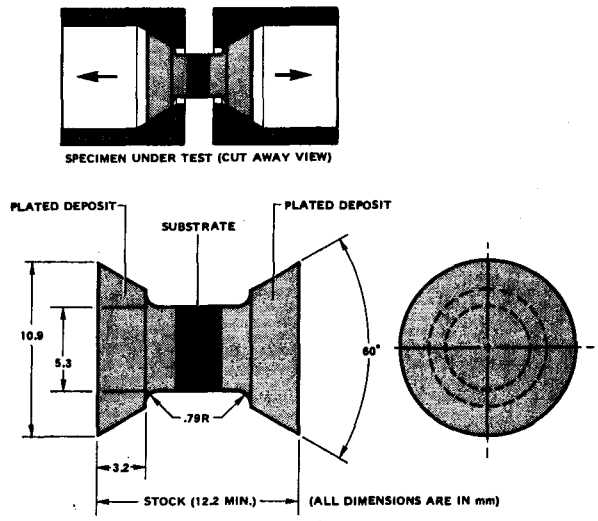

Fig. 2. Conical Head Tensile Specimen

Table I

RING SHEAR DATA FOR U-Ti PLATED WITH COPPER, ELECTROLESS NICKEL, AND NICKEL[1]

Deposit	Plating Solution	MN/m^2	(psi)
Copper	Cu bath HY (sulfate)[2]	100	14,500
Copper	Pyrophosphate[3]	96	14,000
Copper	Same as above, but heated at 260C for one hour in vacuo prior to testing	45	6,500
Electroless Nickel	Enplate Ni-410[4] (preceded by a nickel sulfamate strike)	72	10,500
Electroless Nickel	Enplate Ni-410	33	4,800
Nickel	Nickel sulfamate[5]	200-324	29,000-47,000

[1]All rods were 1/2 inch in diameter. They were etched in solution containing 1400 g/l $FeCl_3 \cdot 6H_2O$ prior to coating.

[2]The Sel Rex Co., Nutley, NJ.

[3]M&T Chemicals, Rahway, NJ.

[4]Enthone, Inc., New Haven, CT.

[5]The Richardson Co., Allied-Kelite Div., Los Angeles, CA.

CONICAL HEAD TESTS, U-Ti

For this work, two different etchants, one containing ferric chloride and the other zinc chloride were used. The data, included in Table II, show that the ferric chloride etchant was noticeably superior to the zinc chloride etchant. The results also clearly emphasize the variations obtainable when mechanical interlocking has to be relied upon for adhesion. In all cases, samples failed at the interface between the uranium and nickel plating. For some of the higher strength bonds, nickel was actually left in disparities in the uranium. Some of the samples were tested a second time so that the strength of the remaining nickel-uranium interface could be determined. This was done by simply grasping the cylindrical uranium portion of the sample in a set of jaws and the other end in one of the dies normally used for testing conical head samples. The data in Table II show that in some instances, the strength of the bond varied noticeably from one side of the sample to the other. For example, with a zinc chloride etchant, one side of one specimen failed at 152 MN/m^2, while the other side failed at 324 MN/m^2. Although the strengths were quite higher when the ferric chloride etchant was used, this same type of variation was noted, e.g., 308 MN/m^2 on one side versus 528 MN/m^2 on the other side of the same sample.

Table II

CONICAL HEAD TENSILE DATA FOR NICKEL PLATED U-0.75 Ti[A]

	Trial 1		Trial 2	
	MN/m^2	(psi)	MN/m^2	(psi)
Zinc Chloride/Nitric Acid[B]	152	22,000	324	47,000
	197	28,500	---	---
Ferric Chloride[C]	331	48,000	---	---
	434	63,000	514	74,500
	396	57,500	---	---
	548	79,500	624	90,500
	620	90,000	---	---
	594	86,000	---	---
	483	70,000	549	79,500
	308	44,500	528	76,500
	662	96,000	---	---

[A] The cleaning/plating cycle consisted of degreasing, scrubbing, and soaking in hot alkaline cleaner, cleaning with detergent, pickling in 8M HNO_3, etching per above, pickling in 8M HNO_3, and nickel sulfamate plating.

[B] The zinc chloride etchant contained 1000 g/l $ZnCl_2$ and 200 ml/l HNO_3. Operating temperature was 22C and etching time was 25 minutes (a 15 minute etch followed by two successive 5 minute etches). Metal removal was 75 μ (3 mils) per side.

[C] The ferric chloride etchant contained 1400 g/l $FeCl_3 \cdot 6 H_2O$. Operating temperature was 49C and etching time was 15 minutes (a 10 minute etch followed by a 5 minute etch). Metal removal was 37 μ (1.5 mils) per side.

The variations in etching characteristics of the material can be clearly seen by comparing Figures 3 and 4 which are cross sections taken from opposite sides of an etched

and plated U-Ti specimen. Although both sides were exposed to the etching solution at the same time, one side etched noticeably different than the other. Figure 3 shows the etch pattern that is most desirable for uranium or its alloys, whereas Figure 4 shows a surface that etched only in selected locations and was virtually untouched in others. The etched surface shown in Figure 3 would most likely result in the higher values reported in Table II, while the surface of Figure 4 the lower values. The reasons for these variations in etching response are not known but thought to be due to variations in the basis metal. Compositional variations, grain size differences, and orientation of the grains are considered to be some of the influencing factors.

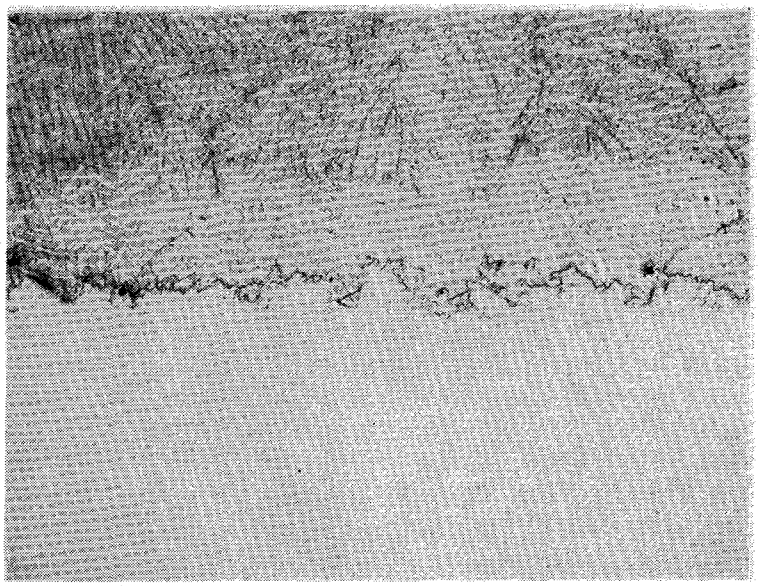

Fig. 3 Side A Mag. 150X

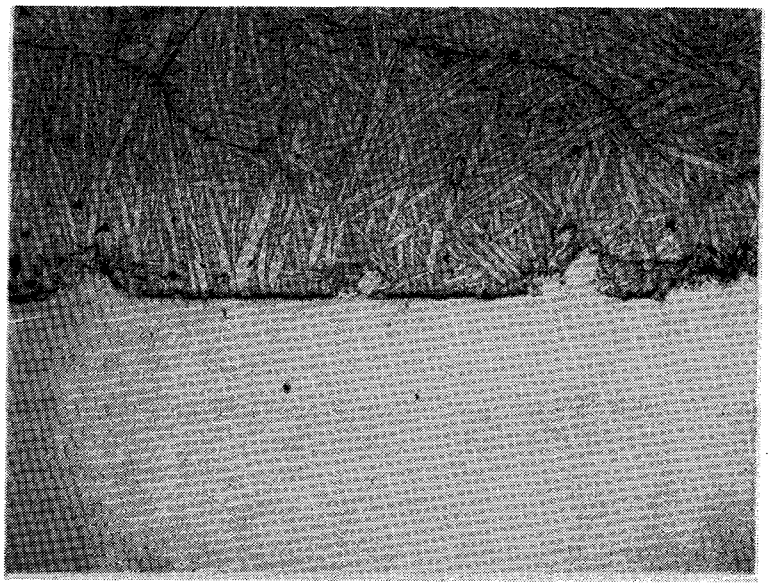

Fig. 4 Side B Mag. 150X

Figs. 3 and 4. Cross Sections of Opposite Sides of an Etched (Ferric Chloride) and Plated U-Ti Specimen

CONICAL HEAD TENSILE TESTS, MULBERRY

Mulberry, a uranium alloy high in alloying constituents (7-1/2% Nb - 2-1/2% Zr) is not etched very readily in the ferric chloride solution (1400 g/l $FeCl_3 \cdot 6\ H_2O$) that works so well with most uranium alloys. The high alloy content of the material which is responsible for its good corrosion resistance makes the alloy difficult to etch. Best etching results with mulberry have been obtained with a solution very dilute in ferric chloride and very concentrated in nitric acid, e.g., 20 g/l $FeCl_3 \cdot 6\ H_2O$, 500 ml/l HNO_3. Initiation of the etching reaction is helped by roughening the surface by sandblasting and then applying by brush coat a solution of 1400 g/l ferric chloride before immersing the part in the etching solution. The ferric chloride precoat helps the etching reaction to initiate more rapidly and uniformly during final etching.

CONICAL HEAD TESTS, MULBERRY

Conical head tensile data were obtained for mulberry which was etched by the process just described prior to nickel plating. After plating, some samples were heated at 260C or 540C for 1 hour prior to testing at room temperature. The results (Table III) show that bond strength was dependent on etch time with better strengths obtained for longer etching times, 456 MN/m^2 after etching for 15 minutes versus 319 MN/m^2 after etching for 10 minutes. As expected, the shorter etching cycle did not produce as rough a surface finish as the longer etch cycle (Table III) and this is undoubtedly the reason for its inferior adhesion.

Heating samples at 260C for 1 hour improved the bond strength at room temperature regardless of the etching conditions used. Heating at 540C for 1 hour reduced bond strengths.

Table III

CONICAL HEAD TENSILE DATA FOR NICKEL PLATED MULBERRY

Etch Conditions[1]	Surface Finish	Heating Conditions	Conical Head[2,3] Strength MN/m^2	Conical Head[2,3] Strength (psi)
20 g/l $FeCl_3 \cdot 6\ H_2O$	430-500 µin, CLA	None	319	22,000[1]
Plus 500 ml/l HNO_3		260C-1 hr	377	26,000
2 each 5 minute etches		540C-1 hr	117	8,100
at 24C				
Same as above, 3	500-600 µin, CLA	None	456	31,500[1]
each 5 minute etches		260C-1 hr	681	47,000
at 24C		540C-1 hr	377	26,000

[1]Prior to etching, all samples were brush coated with a solution containing 1400 g/l $FeCl_3 \cdot 6\ H_2O$.

[2]All samples were tested at room temperature.

[3]Average of 4 tests.

JOINING MULBERRY BY PLATING

The etching procedure previously described for mulberry was further evaluated by using it to prepare mulberry cylinders 76 mm (3 inches) in diameter before joining them by nickel plating to aluminum cylinders. A taper was machined on each cylinder prior to plating. For the aluminum, this taper was consistently kept at 8°32'; for the mulberry it was varied from 17° to 50° to determine influence of the taper angle on joint strength. Parts to be joined were mated and held together while approximately 2.3 mm (90 mils) of nickel was plated at the apex of the joint. Figure 5 shows a mulberry and aluminum part before plating, Figure 6 after plating and machining.

Three parts were tensile tested to failure with the results shown in Table IV. All failed at the nickel plating-mulberry interface (Figure 7) at joint strengths inversely proportional to the taper on the mulberry, e.g., the smaller the taper on the mulberry the higher the joint strength. This wasn't an unexpected finding, since the smaller taper angles provided more bonding surface for mechanical interlocking of the plating.

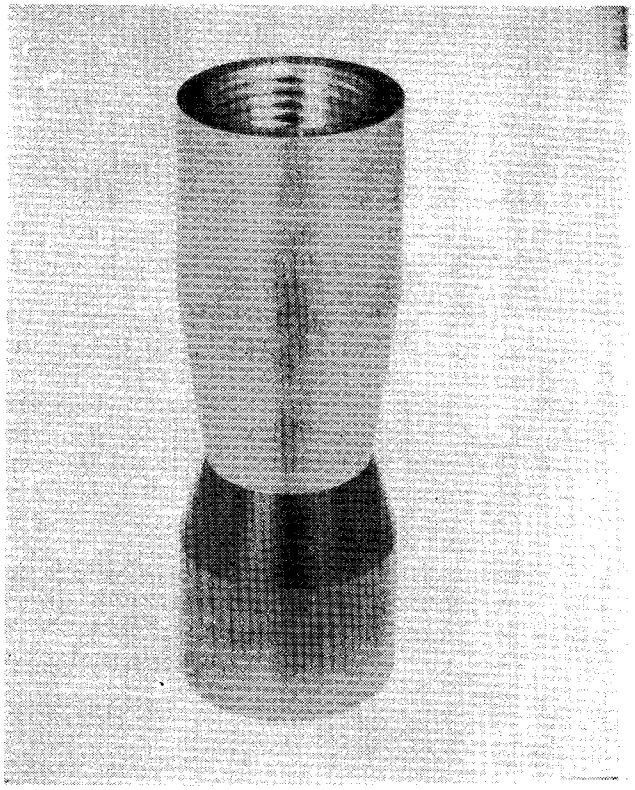

Fig. 5. Aluminum and Mulberry Parts Before Joining by Plating (Al is on top)

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