Plating on Some Difficult-to-Plate Metals and Alloys

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ABSTRACT

Electrodeposition of coatings on metals such as beryllium, beryllium-copper, Kovar, lead, magnesium, thorium, titanium, tungsten, uranium, zirconium, and their alloys can be problematic. This is due in most cases to a natural oxide surface film that readily reforms after being removed. The procedures we recommend for plating on these metals rely on replacing the oxide film with a displacement coating, or etching to allow mechanical keying between the substrate and plated deposit. The effectiveness of the procedures is demonstrated by interface bond strengths found in ring-shear and conical-head tensile tests.

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PLATING ON SOME DIFFICULT-TO-PLATE METALS AND ALLOYS

Introduction

What do beryllium, beryllium-copper, Kovar, lead, magnesium, thorium, titanium, tungsten, tungsten-nickel-iron, uranium, and Zircaloy-2 have in common? They are some of the metals and alloys which require electroplating for corrosion resistance and other purposes, but which are also among the most difficult to plate with sound, functionally acceptable deposits.

The origin of the difficulty is typically a thin naturally forming oxide surface film that is often difficult to remove and that reforms quickly when a cleaned surface is exposed to air or water. As a result, adherent electro-deposits are obtained only when either: (1) the oxide film is removed for a sufficient time to permit an initial deposit, (2) the film is replaced with another that does not interfere with adhesion, (3) the film is incorporated into the deposit in a compatible manner, or (4) the surface is severely etched to allow mechanical keying between the substrate and deposit. It is the purpose of this report to document successful procedures that rely on one or more of the above principles, and to give quantitative information on the range of bond strengths that can be expected from each.

Adhesion Testing

Qualitative adhesion tests cannot be relied upon for definitive judgments about electrodeposits. For example, lack of adhesion is not necessarily manifested in a photomicrograph as a clearly defined gap or layer at the deposit-substrate interface, and similarly thin deposits can give misleading indications if only a simple bend or chisel test is employed. We strongly believe that adhesion should be measured quantitatively through tests in which an effective means of grasping the deposit has been devised and a serious attempt has been made to separate the deposit from the base metal. The data presented in this report were obtained from ring-shear and conical-head tension tests. Both have been described in detail in previously published work along with data showing their usefulness.[1,2]

Briefly, to perform the ring shear test (Figure 1) a cylindrical rod is coated with separate rings of electrodeposit of predetermined width. Follow-ing post plating machining the rod is forced through a hardened steel die having a hole whose diameter is greater than that of the rod but less than that of the rod plus coating. The bond shear strength A (in MN/m^2 or psi)

is determined by the formula $A = W/\pi dt$, where d is the diameter of the rod, t the width of the deposit, and W the force required to cause failure in the specimen.
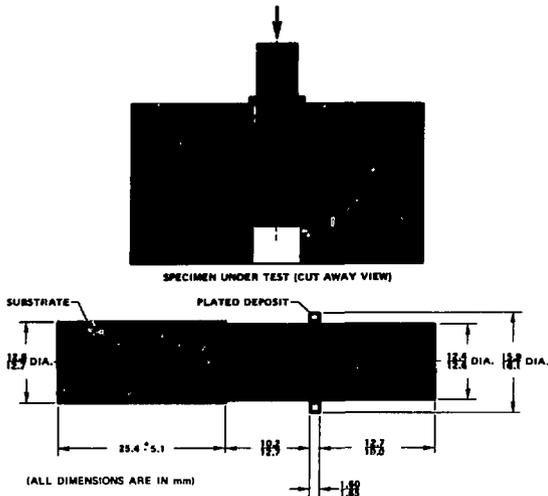
Figure 1. Ring Shear Test Specimen and Die

For the conical-head tension test (Figure 2) flat panels are plated on both sides with thick electrodeposit and conical-head specimens are machined from the panels. The electrodeposit, the substrate, and the bond between the two are tested in tensile fashion, the loading direction being normal to the bonding surface.

Plating Procedures and Bond Strengths

Beryllium

For good adhesion to beryllium it is absolutely essential to apply an adherent immersion zinc deposit (this is called a "zincate treatment") before electrodepositing the primary material of interest. Even knowing this, care must be taken to choose the proper zincate formulation since high pH solutions provide inferior results. Ring shear data (Table I) show that poor adhesion-- less than 60 MN/m^2--is obtained when no zincate treatment is used and also when the pH of the zincate solution is 9.3 or higher. Specimens given a

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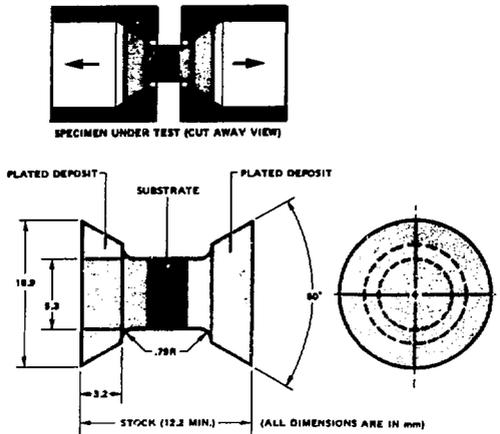
Figure 2. Conical Head Test Specimen

TABLE I

RING SHEAR DATA FOR NICKEL-PLATED BERYLLIUM[a]

Treatment	pH	Shear Strength (MN/m^2)	(psi)
No zincate		0 - 51[c]	0 - 7,400
Zincate[b]	pH 10.7	26	3,700
Zincate	pH 9.3	60	8,700
Zincate	pH 3.0	232	33,700
Zincate	pH 3.2	241	35,000
Zincate	pH 7.7	281	40,800

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[a]Beryllium was S-200-E, 12.7 mm (0.5 in.) diameter rod. The nickel-plating
solution contained 450 g/litre nickel sulfamate, 40 g/litre boric acid, and
1.0 g/litre nickel chloride. Current density was 268 A/m^2 (25 A/ft^2),
pH 3.8 to 4.0, temperature 49°C (120°F), and anodes were SD nickel.
[b]This is typically followed by a strike in a copper cyanide solution
before application of the primary deposit.
[c]Some specimens failed during machining before test.

zincate treatment in solutions ranging from pH 3.0 to 7.7 exhibit shear strengths ranging from 232 to 281 MN/m^2.

Further detail is revealed with conical head testing. Ingot-grade Be which is nickel plated after zincating in a solution at a pH of 3.2 fails in the Be at 166-171 MN/m^2. Heating for as long as four hours at 316°C does not affect bond strength. These data are included in Table II along with a recommended zincate solution formulation. For additional detail on plating on Be the reader is referred to Reference 3.

TABLE II

CONICAL HEAD TENSILE DATA FOR ELECTROPLATED INGOT-GRADE BERYLLIUM[a]

	Tensile Strength (MN/m^2)	(psi)	Location of Failure
As-Deposited	171	24,800	In Be
After heating at 316°C for one hour	158	22,900	In Be
After heating at 316°C for four hours	166	24,100	In Be

[a]The process for preparing the Be for plating included cleaning, acid etching in 20 parts HNO_3, 1 part HF, 20 parts H_2O at 23°C for 5 min, zincating in 30 g/l ZnO, 15 g/l KF and 25 ml/l H_2SO_4 at 27°C for 10 seconds (pH 3.2), copper striking in cyanide solution for 2-3 min at 160 A/m^2, and finally nickel plating in a sulfamate solution.

Beryllium-Copper Alloys

Beryllium-copper alloys are useful because of their unusual physical and mechanical properties. By a simple heat-treating operation they can be hardened from a relatively soft and workable state to levels of strength and hardness beyond those of other copper-based alloys.

For plating on Be-Cu, the literature offers a number of pre-plating techniques ranging from simply treating the alloy as if it were ordinary copper, as Haas[4] observes, to the very detailed procedures of Tweed,[5] which include a number of different pickling steps as well as a vigorous bright dip.

In this report comparisons of two extremes in procedures are presented--a simple HCl pickle and the elaborate process of Tweed--for plating nickel and electroless nickel on Berylco 10* and Berylco 25** in the as-received condition

*Be 0.4-0.7, Co 2.35-2.7, balance Cu
**Be 1.8-2.05, Co 0.18-0.30, balance Cu

TABLE III

ADHESION OF ELECTROPLATED NICKEL AND ELECTROLESS NICKEL-PLATED BERYLLIUM-COPPER

		Shear Strength							
		Electroplated Nickel[c]				Electroless Nickel			
		As-Plated		Heated Before Plating to 400 °C, 5 h		As-Plated		Heated Before Plating to 400°C, 5 h[f]	
Alloy	Cleaning/Actuating Procedure	MN/m²	psi	MN/m²	psi	MN/m²	psi	MN/m²	psi
Berylco 10[d]	HCl Pickle[a]	405	59,600	431	62,400	212;193	30,800 , 28,000	101,407,166	14,600 , 59,000 , 24,000
Berylco 10[d]	Tweed Process[b]	415	60,200	378	54,800	---	---	---	---
Berylco 25[e]	HCl Pickle[a]	431	62,400	385	55,800	414;40D	60,000 , 58,000	222; 229	32,200 , 33,200
Berylco 25[e]	Tweed Process[b]	434	62,800	423	61,200	---	---	---	---

[a]Degrease, caustic-soak, pumice-scrub, anodic-treat in Oakite 90 for 2 minutes at 268 A/m², 1 minute in 18% (by wt) HCl, nickel sulfamate or electroless nickel-plate to thickness.

[b](Reference 5) Degrease; caustic-soak; pumice-scrub; anodic-treat in alkaline cleaner for 2 minutes at 268 A/m²; fluoboric acid (48%) 12 parts, H_2O 88 parts, 1 minute at 60°C; H_2SO_4 (66° Baume) 25 parts, H_2O 75 parts, 1 minute at 56°C; bright-dip 515 ml H_3PO_4, 189 ml HNO_3, 24 ml acetic, 5.25 ml HCl, 17.5 ml H_2O for 20 s at 66°C; fluoboric acid for 30 s at 60°C; KCN 50 g/l for 15 s at room temperature; nickel sulfamate or electroless nickel-plate to thickness.

[c]Each reported value is the average of five separate specimens from one rod.

[d]Shear strength of Berylco 10 was 484 MN/m² (70,400 psi); after heating at 400°C for 5 hours, 495 MN/m² (71 400 psi).

[e]Shear strength of Berylco 25 was 362 MN/m² (52,400); after heating 400°C for 5 hours, 735 MN/m² (106 500).

[f]Each reported value is the average of 10 separate specimens.

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as well as after heating at 400°C for 5 hours. The results (Table III) show
that both work quite effectively. With electroplated nickel, typical bond
strengths average 415 MN/m^2, with failure occurring partially in the nickel
and partially at the interface between substrate and deposit. Similar
results are obtained for specimens heated at 400°C for 5 hours before plating.

For electroless nickel plating only the HCl pickle was examined,
the assumption (on the basis of the above) being that the other techniques
would not give significantly different results. Table III illustrates that
the adhesion is usually not as good as with electroplated nickel. For the
Berylco 10 alloy, strengths are only about one-half those obtained with
electroplated nickel, whereas for Berylco 25 the strengths are nearly equal
to the latter. After being heated at 400°C for 5 hours, plated samples
of both alloys show noticeably reduced bond strengths. Moreover, data
scatter can be large; results with Berylco 10 varied from 101 to 407 MN/m^2.
By contrast, strengths for electroless-plated Berylco 25, given the same heat
treatment before plating, can be expected to be consistently around 225 MN/m^2.

Kovar

Kovar (53 Fe, 29 Ni, 17 Co) was developed specifically for sealing to
glass in vacuum or pressure-tight devices such as electron tubes. It is
quite often plated with gold using relatively standard techniques.[6] Data
are presented here for nickel as well as gold, since the former may be of
interest in some applications.

A number of treatments were evaluated for use prior to gold plating:
(1) sulfuric acid pickle, (2) hydrochloric acid pickle, and (3) Wood's nickel
strike.[7] In the ring shear tests to date, only enough gold was plated to ensure
a diameter greater than that of the die diameter, the rest of the ring being
plated over with copper to increase the thickness up to 1.3 - 1.5 mm. For the
rod plated with nickel, only the hydrocloric acid treatment was evaluated.

The ring shear data (Table IV) clearly show that all treatments work
quite well. In all cases, failure can be expected to occur in either the
gold or nickel deposits, rather than at the interface between the plating
and the Kovar.

Lead

Ring shear tests were used to evaluate a procedure for plating lead over
an already electroplated lead surface. The ASTM recommended practice for
plating on lead and its alloys[8] suggests pickling in solutions containing
either HF or HBF_4. Hence if the plating solution contains a substantial
amount of fluoboric acid (HBF_4), simple immersion of cleaned parts in the
solution will suffice. We recommend immersion in the lead plating solution
for 2 minutes before application of current. There is no apparent benefit to
special cleaning of parts prior to plating. Parts can be expected to fail in
the lead plating at strengths between 11.7 and 12.4 MN/m^2, the ring shear
strength of solid, electroformed lead.

TABLE IV

ADHESION OF ELECTROPLATED GOLD AND NICKEL ON KOVAR

Treatment[A]	Deposit	Shear Strength[B] (MN/m^2)	(psi)	Location of Failure
1. H_2SO_4 Pickle	Gold	152	22,000	In the gold deposit
2. HCl Pickle	Gold	163	23,700	In the gold deposit
3. H_2SO_4 Pickle plus Wood's Nickel Strike	Gold	169	24,500	In the gold deposit
4. HCl Pickle	Nickel	403	58,500	In the nickel deposit

[A]In all cases except 4, gold plating of 0.076 - 0.102 mm was followed by 1.27 - 1.52 mm of copper. For more details on treatment procedures see J. W. Dini and H. R. Johnson, Metal Finishing 72, 44 (Aug. 1974).
[B]Average of five tests for each condition.

Magnesium

A zinc immersion treatment is recommended as the first step for plating on magnesium. After this, a 2-5 µm thick electrodeposit of copper should be applied from a cyanide-type solution. This can then be followed by any metal capable of being deposited from solution. Use of an acid pickle prior to zincating can provide even better bond strengths (145 MN/m^2 vs. 113 MN/m^2 with no acid pickle - Table V). Ring shear tests show failures at the interface between the substrate and deposit (for comparison purposes, the shear strength of solid ZK 60 alloy is 193 MN/m^2). Heating samples for 2 hours at 150°C prior to testing does not affect the bond strength.[9]

Nickel

It is necessary to plate nickel on nickel for many applications, including repairing of rejected parts, plating parts that have to be removed from the plating solutions for machining, continuing plating after current interruptions, and building up worn nickel-plated parts. All these cases require special preparations to remove the oxide film and provide a surface for good adhesion between the layers of nickel. Three activation procedures--Wood's nickel strike, anodic treatment in sulfuric acid, and anodic treatment in sulfamic acid--are evaluated here (Table VI). All work very well, as is evident from the table. The strength levels at which failure occurs for all three treatments (greater than 710 MN/m^2) are representative of what would be expected for solid, electroformed nickel.

TABLE V

RING SHEAR DATA FOR NICKEL-PLATED ZK60 MAGNESIUM ALLOY

Activation-Plating Cycle[a]	Bond Strength[b] (MN/m^2)	(psi)
1. Clean zincate, copper strike, nickel plate	113	16,400
2. Clean, immerse in 100 g/1 ethylenediamine tetra/methylphos-phonic acid, pH 6.0-7.3, zincate, copper strike, nickel plate	143	20,700
3. Clean, immerse in 5% HNO_3, zincate, copper strike, nickel plate	145	21,000

[a]The zincate solution contained 40 g/1 $Zn_2P_2O_7 \cdot 7H_2O$, 200 g/1 $Na_4P_2O_7 \cdot 10H_2O$ and 16 g/1 $KF \cdot 2H_2O$. Temperature was 72°C, pH 10.0, and immersion time 2 min. The copper strike contained 41 g/1 copper cyanide, 49 g/1 sodium cyanide, 30 g/1 sodium carbonate, 60 g/1 Rochelle Salts; temperature was 38°C and pH 10.3. Nickel plating was done in a sulfamate solution.
[b]The ring shear strength of a ZK 60 rod is 193 MN/m^2 (28,000 psi).

TABLE VI

CONICAL HEAD TENSILE DATA FOR NICKEL-PLATED NICKEL

Process	Tensile Strength (MN/m^2)	(psi)
Wood's Nickel Strike 540 A/m^2, 5 min	711	103,000
Anodic in 400 ml/1 H_2SO_4, 1080 A/m^2, 3 min	762	110,000
Anodic in 100 g/1 sulfamic acid, 1080 A/m^2, 3 min	752	109,000

Thorium

Procedures were evaluated for applying copper and nickel electrodeposits on thorium. The best results were obtained by using a modification of a procedure developed by Beach and Schaer,[10] wherein the thorium is given a series of treatments which serve to etch or roughen its surface prior to plating. The modified process includes: (1) vapor degrease, (2) caustic clean (3) rinse, (4) pickle in 830 ml/1 HNO_3 plus 2 ml/1 HF at room temperature

for 10 minutes, (5) rinse, (6) anodic etch in 100 ml/l HCl at 538 A/m^2 for 5 minutes at room temperature, (7) rinse, (8) step 4 repeated, (9) rinse, (10) pickle in 200 ml/l sulfuric acid for 3 minutes at 45-50°C, (11) rinse, (12) electroless nickel plate for 30 minutes at 88 to 93°C in a solution containing 30 g/l nickel acetate, 10 g/l sodium hypophosphite, 100 g/l sodium citrate, and 50 g/l ammonium acetate, with the pH adjusted to 9.0 with ammonium hydroxide, and (13) electroplating with the desired coating.

The metal removed by this process amounts to about 25 μm (1 mil) per side. Ring shear data for copper or nickel plating are shown in Table VII. The ring shear strengths are very close to that of solid thorium rods.

TABLE VII

RING SHEAR DATA FOR COPPER- AND NICKEL-PLATED THORIUM

| Plated Coating | Ring Shear Strength | |
	(MN/m^2)	(psi)
Copper[a]	118	17,100
Nickel[b]	125	18,100
Nickel[c]	146	21,200
Solid Thorium Rods	175	25,300

[a]Plated in UBAC (Udylyte Corp., Detroit, MI) copper sulfate solution at 107 A/m^2.
[b]Plated in nickel sulfamate solution at 107 A/m^2.
[c]Plated in nickel sulfamate solution at 321 A/m^2.

Titanium

After evaluating many procedures,[11] we concluded that the most promising processes for plating nickel on titanium and some of its alloys include (1) a Pratt & Whitney procedure which includes anodic etching in acid solution prior to heating[12] and (2) a proprietary process marketed by Ionitech Laboratories, Chappaqua, New York. Anodic etching in hot concentrated HCl or chromic chloride plus HCl also provides good adherence but these treatments are not very practical. Ring shear data are presented in Table VIII for a number of alloys.

Tungsten

The procedure we evaluated for tungsten is taken from Marzano.[13] The crucial step in the process (according to Marzano) is anodic treatment in a hot solution of 30% KOH. Our data for nickel plating (Table IX) show very low ring shear adhesion values for this process. Improved adhesion could be obtained from a chromium strike prior to nickel plating. Marzano claims that it is quite critical that a strike deposit be used when the main electro-

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TABLE VIII

RING SHEAR DATA FOR NICKEL PLATED TITANIUM ALLOYS

Process	Alloy	Ring Shear Strength MN/m^2	psi
Pratt & Whitney[1]	6A1-4V	148	21,500
Ionitech[2]	6A1-4V	131	19,000
CrCl$_3$-HCl-H$_2$O[3]	6A1-4V	177	25,600
CrCl$_3$-HCl[4]	6A1-4V	166	24,000
HCl[5]	6A1-4V	89-266	21,700-43,300
Pratt & Whitney[1]	5A1-2.5 Sn	100	14,600
CrCl$_3$-HCl[4]	5A1-2.5 Sn	25	3,600
Pratt & Whitney[1]	6A1-6V-2.5Sn	72	10,500
CrCl$_3$-HCl[4]	6A1-6V-2.5Sn	136	19,700
Pratt & Whitney[1]	Commercially Pure Ti	100	14,600

1. The Pratt & Whitney process included abrasive blast, clean in hot alkaline solution, HCl pickle, bright dip in 12% (vol.) HF (70%), 1% HNO$_3$, balance H$_2$O, anodic etch 6 min, 162 A/m^2, 40°C in 13% (vol.) HF (70%), 83% acetic acid, 4% H$_2$O plate with 25 μm of nickel in a sulfamate solution, heat at 48°C for 2 hours, plate with about 0.5 mm of nickel.
2. Proprietary process of Ionitech Laboratories, Chappaqua, New York.
3. Anodic in 210 g/l CrCl$_2$·6H$_2$O plus 100 ml/l HCl, 10,000 A/m^2, 5 min, 100°C.
4. Anodic in 210 g/l CrCl$_3$·6H$_2$O diluted to one liter with conc. HCl (37 wt.%), 6000 A/m^2, 10 min. 100°C.
5. Anodic in conc. HCl (37 wt.%), 1000 to 10,000 A/m^2, 5 to 10 min, 90-100°C.

plate has expansion characteristics differing considerably for those of tungsten. Since the coefficients of thermal expansion of W, Ni, and Cr are 4.6, 13.0, and 6.2 cm/cm°C, respectively, the potential value of an intermediate layer of chromium is evident.

Tungsten-Nickel-Iron Alloy

This alloy typically contains 95% W with the balance being Fe and Ni. After fabrication, about 50-60% of the W is in the free state with the balance tied up as a W-Ni-Fe alloy. For this reason it can be expected that better adhesion results will be obtained with this material than with pure W. The suggested pre-plating procedure consists of etching in a solution containing HF and HNO$_3$. The nickel-plating results (Table IX) show that regardless of the temperature of the etch, much better results are obtained with this alloy than with pure W. Use of the etch at 22°C provides less bond strength than when the etch is used at 50°C. This is because at the higher temperature the etched surface is considerably rougher, thus providing more sites for interlocking of the subsequent deposit.

TABLE IX

ADHESION DATA FOR TUNGSTEN AND TUNGSTEN-NICKEL-IRON ALLOY[a]

Material			Activation Procedure	Ring Shear (MN/m^2)	(psi)	Conical Head (MN/m^2)	(psi)
				Bond Strength			
Tungsten	A.	1.	Clean				
		2.	Etch in 3 parts HF, 1 part HNO_3, and 4 parts H_2O for 5 min at 22°C.	16	2,300	--	--
		3.	Treat anodically in 300 g/l KOH at 50°C and 1076 A/m^2 for 5 min.				
		4.	Nickel plate				
Tungsten	B.	1.	Clean	22	3,200	--	--
		2.	Etch in 3 parts HF, 1 part HNO_3, and 4 parts H_2O for 5 min at 50°C.				
		3.	Nickel Plate				
Tungsten-Nickel-Iron	C.		Same as A above	169	24,500	83	12,000
Tungsten-Nickel-Iron	D.		Same as B above	235	34,000	128	18,500

[a]The alloy contains 95% W with the balance being Ni and Fe.

Uranium and Uranium Alloys

Metallic coatings such as nickel are used to provide corrosion resistance for uranium, which is readily oxidized in air by water vapor even at room temperature. Because of uranium's tendency to oxidize, true chemical bonding is difficult to obtain between electrodeposits and uranium. Therefore, the uranium surface must be roughened by either chemical, electrolytic, or mechanical means to provide some degree of mechanical adhesion. The most successful techniques involve chemical or electrolytic treatment in acid solutions containing chloride ion followed by removal of chloride reaction products in nitric acid before plating (Fig. 3). The process we prefer for unalloyed uranium consists of etching in a solution containing 1400 g/l ferric chloride.[14]
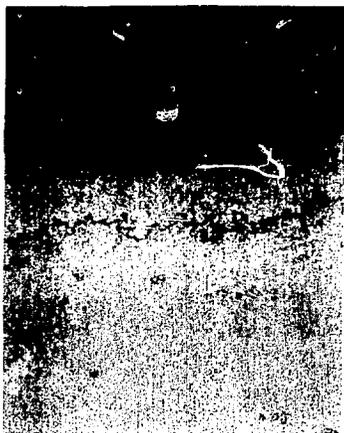
Figure 3. Cross Section of Unalloyed Uranium After Etching In Ferric
Chloride Solution and Plating With Nickel

The above comments regarding passivity are even more applicable with
uranium alloys, which contain various alloying elements for improving corrosion
resistance and mechanical properties. As a rule of thumb, the higher the
alloy content, the harder it is to etch the alloy satisfactorily for plating.

Good bond strengths (e.g., greater than 200 MN/m^2) are obtainable for
all samples plated with nickel (Table X). The highest values are found with
unalloyed uranium. Poor bond strengths (less than 100 MN/m^2) were obtained when
copper is used as the plating material. The reason(s) for the superiority of
nickel over copper is not known; however, this result is consistent with
observations made at Sandia with unalloyed uranium over the past 15 years.

Good adhesion is obtained when U-0.75 wt% Ti and U-2.25 wt% Nb are
etched in a ferric chloride solution; even better results are obtainable with
a zinc chloride/ nitric acid etchant. This latter etch provides a very rough
surface (∼ 500 μin CLA vs 100 μin. CLA for ferric chloride). The U-6 wt% Nb
alloy occasionally reacts explosively in solutions containing nitric acid and
it is not attacked very readily by ferric chloride, so we suggest etching it
anodically in a sulfuric acid/hydrochloric acid solution. Mulberry (U-7.5
wt% Nb, 2.5 wt% Z.) can be successfully etched in a solution containing 20
g/l ferric chloride and 500 ml/l nitric acid. With this alloy it is also
imperative that a sand-blasting or roughening treatment be used before the
etching step. For more detail on plating on uranium see References 14-18.

TABLE X

RING SHEAR DATA FOR PLATED URANIUM AND SOME OF ITS ALLOYS

Substrate	Etchant	Deposit	Ring Shear Strength (MN/m^2)	(psi)
Uranium	Ferric Chloride[a]	Nickel	371	53,800
Uranium	Ferric Chloride	Copper	96	14,000
Uranium	Ferric Chloride	Electroless Nickel	329	47,800
U-0.75 wt% Ti	Ferric Chloride[b]	Nickel	247	35,800
U-0.75 wt% Ti	Zinc Chloride[c]	Nickel	330	47,700
U-2.25 wt% Nb	Ferric Chloride[b]	Nickel	201	29,100
U-2.25 wt% Nb	Zinc Chloride[d]	Nickel	314	45,600
U-6.0 wt% Nb	H_2SO_4/HCl[e] H_2SO_4/HCl[f]	Nickel Nickel	242 277	35,000 40,200
U-7.5 wt% Nb-2.5 wt% Zr[h]	Ferric Chloride[a]	Nickel	103	15,000
U-7.5 wt% Nb-2.5 wt% Zr[h]	Ferric Chloride/ Nitric Acid[g]	Nickel	233	33,800

[a]1400 g/l ferric chloride ($FeCl_3 \cdot 6H_2O$), 10 min, 43°C
[b]1400 g/l ferric chloride, 15 min, 49°C
[c]1000 g/l zinc chloride plus 200 ml/l nitric acid, 10 min, 22°C
[d]Same composition as c but 30 min at 49°C
[e]Anodic in 100 ml/l H_2SO_4 plus 10 ml/l HCl, 538 A/m^2, 5 min, 22°C
[f]Same as e but 10 min instead of 5 min.
[g]20 g/l Ferric chloride plus 500 ml/l nitric acid, 5 min, 60°C, 5 cycles of etching and scribbing.
[h]Mulberry

Zircaloy-2*

Zirconium and its alloys form a tenacious oxide very quickly in air. Although the thickness of this oxide is probably less than 25 A, it renders the metal quite passive.[19]

*Zircaloy-2 contains 1.5 Sn, 0.13 Fe, 0.10 Cr, 0.05 Ni, with the balance Zr.

The best results for Zircaloy-2 are obtained when it is etched in ammonium bifluoride solution prior to nickel plating. However, even with this treatment alone, low and inconsistent strengths are found (e.g. 6 to 31 MN/m^2; Table XI). There is a noticeable improvement in bond strength (140-292 MN/m^2) when specimens etched in ammonium bifluoride or ammonium bifluoride/ sulfuric acid solution are heated in a constrained condition at 700°C for 1 hour after plating. We use a TZM molybdenum ring around the plated parts. Since the coefficient of thermal expansion for molybdenum is lower than that of zirconium or nickel, it provides constraint as the assemblies are heated, but only if the clearance between the sample and the die is 25 µm or less. Another successful procedure consists of threading the zirconium prior to plating; strengths with this technique vary from 115 to 269 MN/m^2 (Table XII).[20]

TABLE XI

INFLUENCE OF HEATING ON THE RING SHEAR STRENGTH
OF NICKEL-PLATED ZIRCALOY-2[a]

Activation Treatment	As-Deposited MN/m^2 (psi)	700°C, 1 hr (unconstrained) MN/m$_2$ (psi)	700°C, 1 hr (constrained)[b] MN/m^2 (psi)
1. Vapor degrease			
2. Cathodic alkaline clean	16 (2300)		140 (20,300)
3. Immersion in 15 g/l ammonium bifluoride, 1/2 ml/l H$_2$SO$_4$, 1 min at 22°C	25 (3600)	38 (5500)	292 (35,000)
	15 (2100)		224 (32,500)
4. Nickel plate			
1. Vapor degrease			
2. Cathodic alkaline clean	31 (4500)	38 (5500)	235 (34,100)
3. Immersion in 45 g/l ammonium bifluoride, 3 min at 22°C	6 (800)	12 (1700)	234 (34,000)
			190 (27,500)
4. Nickel plate			

[a]Each reported value is the average of at least two tests.
[b]A TZM molybdenum ring is used to constrain the specimens during heating. Clearance between the specimens and ring is 25 µm or less on the diameter.

TABLE XII

RING SHEAR DATA FOR MECHANICAL PREPARATION TREATMENTS FOR ZIRCALOY-2

Description	Process Details	Ring Shear Strength (MN/m^2)	(psi)
Threaded Surface	Surface threaded, 52 threads per 2.54 cm, 0.13 mm (5 mils) deep, plated with electroless nickel	122	17,600
Threaded Surface	Same as above, but plated with silver	184	26,700
Threaded Surface	Same as above, but plated with nickel	199	28,800
Threaded Surface	Same as above, but threads were 0.26 mm (10 mils) deep	269	39,000
Threaded Surface	Same as above, but plated with chromium	255	37,000
Knurled Surface	Knurled surface machined on rod, then plated with nickel	115	16,700

Summary

The procedures we recommend for plating on a number of difficult to plate metals and alloys, i.e., beryllium, beryllium-copper, Kovar, lead, magnesium, thorium, tungsten, uranium, zirconium have been described. In most cases the treatments involve replacing the oxide film with a displacement coating or etching to allow mechanical keying between the substrate and plated deposit. This is not to say that these procedures are the only methods for plating adherently on the metals described. However, the effectiveness of our procedures was demonstrated by quantitative adhesion tests wherein the deposit-substrate combination was tested in both shear and tensile modes.

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