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Plating on Zircaloy-2

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ABSTRACT

Zircaloy-2 is a difficult alloy to coat with an adherent electroplate because it easily forms a tenacious oxide film in air and aqueous solutions. Procedures reported in the literature and those developed at SLL for surmounting this problem were investigated. The best results were obtained when specimens were first etched in either an ammonium bifluoride/sulfuric acid or an ammonium bifluoride solution, plated, and then heated at 700 C for 1 hour in a constrained condition. Machining threads in the Zircaloy-2 for the purpose of providing sites for mechanical interlocking of the plating also proved satisfactory.

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PLATING ON ZIRCALOY-2

Introduction

Zirconium is one of a group of metals including Be, Al, Ti, Nb, Mo, Th, and U, whose properties are important in certain nuclear applications. Like many of these metals, zirconium's surface properties are such that soldering and brazing to a second metal are difficult. Coating the zirconium with another metal by electroplating has sometimes been used to surmount this difficulty. Schickner, Beach, and Faust¹ have shown that nickel electroplates on Zr can withstand a soldering operation.

However, zirconium is a difficult metal on which to make an adherent plating because it forms a tenacious oxide very quickly in air. Although the thickness of this oxide is probably less than 25 Å,² it renders the metal quite passive. In this regard zirconium is not unlike Be, Al, Mg, and stainless steels, all of which require special activation treatments if a plating is to be adherent.

At Sandia we have had considerable experience joining metals by plating when other means were difficult to use.^{3,4} In one particular application it was necessary to join zirconium and stainless steel. The desired service temperature was around 350 C, and silver brazing did not produce acceptable results. It was therefore decided to investigate a number of plating procedures with the ultimate goal being to provide a capability for joining zirconium to other metals by plating:

Review of the Literature

The literature on plating on zirconium is relatively sparse. Researchers at Battelle Columbus Laboratories have been the most prolific in this area.^{1,5-7} Schickner, Beach, and Faust¹ utilized a process consisting of chemical polishing followed by etching in ammonium bifluoride/hydrofluoric acid solution prior to nickel plating. For best bonding, parts were then prebaked at 200 C for 2 to 4 hours and then heated at 700 C for 10 to 45 minutes. Other metals could then be deposited on the nickel. Another technique they used consisted of applying an immersion zinc plate by dipping zirconium for 1 minute in molten zinc chloride at 440 to 450 C.⁵ Silver soldering of a brass rod to the zinc-coated zirconium resulted in a joint that did not fail until after the rod was severely bent. Tripler, Beach, and Faust⁷ studied methods of coating zirconium with platinum for the purpose of decreasing the corrosion in uranyl sulfate solutions. The

chemical polishing procedure followed by the ammonium bifluoride/hydrofluoric acid etch discussed above was used with subsequent diffusion bonding.

Huddle and Flint⁸ prepared zirconium for plating by shot blasting and then immersing it in a solution of copper sulfate, aluminum sulfate, and sulfuric acid. The immersion copper film formed by this process could then be plated over with other metals. Charveriat⁹ protected zirconium and its alloys by applying a chromium deposit from a solution containing chromic acid, strontium sulfate, and potassium fluosilicate. He claimed improved adhesion and ductility of this coating by vacuum heating at 700 to 850 C. Kneip and Turnbaugh¹⁰ patented a procedure for copper plating on Zr-Nb alloys, with HF, ferric chloride, and nickel chloride. Saubestre¹¹ utilized the "hydride plating process", which consists of room-temperature cathodic treatment for 5-15 seconds at 108-1080 A/m² (10-100 asf) in electrolytes such as 2%(wt.) HCl, H₂SO₄, HNO₃, HF, KOH, or NaOH.

Kohan¹² described the immersion plating of Zircaloy-2 with copper, iron, tin, or nickel in solutions containing hydrofluoric acid. Very recently, Wax and Cowan¹³ patented the use of solutions comprised of dilute amounts of ammonium bifluoride and sulfuric acid for activating zirconium for plating.

Test Procedures

The material used was Zircaloy-2 in the shape of 1.27-cm-diameter rods.* Several procedures, for which the detailed formulations and conditions are listed in Table I, were evaluated. Quantitative data were obtained for these processes by use of ring shear tests. These consisted of coating the rods with separate rings of plating of predetermined width and then forcing the specimen 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 were used to calculate strength. Complete details on ring shear sample preparation and test procedures have been described elsewhere.¹⁴⁻¹⁵ Unless otherwise mentioned, nickel deposited from a sulfamate solution (Table II) was used for the coating we were trying to deposit adherently on the Zircaloy.

Based on the results of this phase of the program, some samples were then prepared for heat treatment studies to determine if this would help improve adhesion. In addition, other samples were given mechanical treatments such as threading or knurling for the purpose of increasing surface area of the Zircaloy.

* Zircaloy-2 contains 1.5 Sn, 0.12 Fe, 0.10 Cr, 0.05 Ni, 0.01 O, with the balance Zr.

TABLE I
RING SHEAR DATA FOR CHEMICAL ACTIVATION TREATMENTS FOR ZIRCALOY-2

Description	Reference	Process	Ring Shear Strength ^a	
			(MN/m ²)	(psi)
Ammonium Bifluoride	1	Etch in 45 g/l ammonium bifluoride, 3 min at 22 C	81	11,800
			31	4,500
			8	800
Ammonium Bifluoride/ Sulfuric Acid	13	Etch in 15 g/l ammonium bifluoride, 1/2 ml/l sulfuric acid, 1 min at 22 C	78	11,400
			25	3,600
			15	2,100
Ammonium Bifluoride/ HF	1	Etch in 50 g/l ammonium bifluoride, 5 min at 50 C	17	2,500
			31	4,500
Copper Nitrate/HF	12	Immerse in 50 g/l copper nitrate, 3 ml/l HF, 37 C, 1 hr	39	5,700
Sodium Hydroxide	-	Use anodic oxidation in 100 g/l NaOH at 5 V, 10 min, 25 C	37	5,300
HF, Ferric Chloride, Nickel Chloride	10	Pickle in 100 ml/l HF, 4 g/l ferric chloride, 3 g/l nickel chloride, 20 s at 22 C; then use copper strike before final plating	48	7,000
Ionitech Process	16	Pickle in 200 ml HNO ₃ , 100 ml H ₂ SO ₄ , 100 ml H ₂ O, 45 g actane 70, 5 min; then immerse in 20% HNO ₃ at 80 C prior to nickel plating	26	3,800
Wood's Nickel	17	Use Wood's nickel strike, cathodic, 5 min at 540 A/m ²	23	3,300
H ₂ SO ₄ /Wood's Nickel	-	Use anodic oxidation in 70% (wt.) H ₂ SO ₄ , 3 min at 1080 A/m ² followed by Wood's nickel, cathodic, 5 min at 540 A/m ²	17	2,500
Cobalt Sulfate Strike	18	Etch in 50 g/l ammonium bifluoride, 30 ml/l HF, 5 min at 50 C, strike in 200 g/l CoSO ₄ · 7 H ₂ O, 80 ml/l H ₂ SO ₄ at 22 C, 5 min at 540 A/m ²	22	3,200
Ammonium Bifluoride/ Wood's Nickel	-	Etch in 45 g/l ammonium bifluoride, 3 min at 22 C, then 50% HNO ₃ , 3 min, then Wood's nickel, 5 min at 540 A/m ²	10	1,500
Hydride Process	11	Etch in 10% HF, 2 min; cathodic for 15 s at 1080 A/m ² in 2 g/l NaOH	10	1,500

^a Each value is the average of at least three tests. All specimens were overplated with nickel using the formulation and conditions listed in Table I.

TABLE II
COMPOSITION AND OPERATING CONDITIONS FOR
NICKEL SULFAMATE SOLUTION

Nickel (as nickel sulfamate*)	81 g/l
Nickel chloride	<1.0 g/l
Boric acid	40 g/l
Surface tension	38 dyne/cm
pH	3.8 - 4.0
Anodes	Sulfur depolarized
Current density	215 A/m ²
Temperature	49 C

* M&T Chemicals, Rahway, NJ

Results

A. As Deposited

The data for the chemical activation treatments which resulted in adhesion measurable by the ring shear test are presented in Table I. The best results--81 MN/m² (11,800 psi)--were obtained when specimens were etched in ammonium bifluoride solution prior to nickel plating. However, the data for these were inconsistent inasmuch as values ranging from 6 to 81 MN/m² were obtained. Activation in a solution containing HF, ferric chloride, and nickel chloride gave good results (48 MN/m²). All the other techniques resulted in strengths less than 40 MN/m². For comparison, the ring shear strength of solid Zr-2 is 362 MN/m².

Other processes evaluated were anodic treatment in concentrated HCl, immersion in ferric chloride/HF, anodic treatment in ammonium bifluoride/HF prior to chromium plating, and anodic treatment in an iodine/methanol solution. They were not effective. Ring shear specimens could not be successfully machined from specimens given these treatments prior to plating, thus indicating that the plating-substrate bond was essentially nonexistent.

Although the results with ammonium bifluoride were uneven, additional work was done with this etchant since it offered more promise for use in production because of its simplicity when compared to the other processes listed in Table II.

B. After Heating

Other workers have reported on the beneficial effects of diffusion to improve adherence.¹⁻⁶ Based on their work, specimens were activated in ammonium bifluoride, nickel plated, and then heated in vacuum at 700 C in both constrained and unconstrained conditions. One set of constrained specimens were placed in a TZM molybdenum ring during heating. Since the coefficient of thermal expansion for molybdenum is lower than that of zirconium or nickel, it provided a stress on the plating as the assemblies were heated. Zanner and Fisher¹⁹ used this approach to bond bronze successfully to a titanium alloy.

Because of the importance of this technique, an analysis was made of the differential thermal constraint of the Zr-Ni-Mo composite. The problem, shown schematically in Figure 1, is one of concentric cylinders with clearance gaps closing with increasing temperature, thereby producing compressive stress at the bond line. The material properties that were used for the calculation are listed in Table III. A finite element analysis was done in which the cylinders were uniformly heated in steps to 700 C. The zero-stress temperature was 25 C. The clearance for this problem must be very small to produce a substantial compression at the bond. For calculational purposes, initial clearances were varied from 0 (no clearance) to 50 μm (for this value, contact between the cylinders did not take place at 700 C--see Figure 2).

Figure 1. Schematic of Parts

TABLE III
PROPERTIES OF THE MATERIALS USED IN
DIFFERENTIAL THERMAL ANALYSIS

	Coefficient of Linear Thermal Expansion (10^{-6} cm/cm °C)	Modulus of Elasticity (10^4 MN/m ²)
Ni	15.0	172
Mo	5.4	324
Zr	8.0	95

Figure 2. Radial Stresses as a Function of Radius for a
Zr-Ni-Mo Composite at 700 C

Several points are worth noting. (1) The stresses at the zirconium-nickel interface are only compressive for a very tight fit (initial clearances less than 25 μm). (2) The maximum compressive stress that can be developed is about 262 MN/m^2 (38,000 psi) with a perfect initial fit. Larger starting clearances than this produce a reduced bond stress. (3) Tensile stresses can be present in the joint even with some interference. For example, refer to the 25- μm curve in Figure 2, in which $\sigma_{rr} > 0$ for $r < 0.69$ cm. This is caused by the nickel expanding away from the zirconium. (4) For any initial nonzero clearance, as the temperature increases and while the cylinders are not in contact, the inner cylinder will develop tensile stress at the bond interface.

Results of the heating experiments are presented in Table IV. The data clearly show a noticeable improvement as a result of heating for specimens which were constrained during heating (the clearance between the cylinders and the Mo die was 25 μm or less for all of this work). Bond strengths around 240 MN/m^2 were obtained for a number of specimens. For comparison purposes, the shear strength of electroformed sulfamate nickel after heating at 700 C for 1 hour is 310 MN/m^2 .

TABLE IV
INFLUENCE OF HEATING ON THE RING SHEAR STRENGTH
OF NICKEL-PLATED ZIRCALOY-2^(a)

Activation Treatment	As-deposited	Ring Shear Strength, MN/m^2 (psi)	
		700 C, 1 hr (unconstrained)	700 C, 1 hr (constrained) ^(b)
1. Vapor degrease	16 (2300)	38 (5500)	292 (35,000)
2. Cathodic alkaline clean			
3. Immersion in 15 g/l ammonium bifluoride, 1/2 ml/l H_2SO_4 , 1 min at 22 C			
4. Nickel plate	15 (2100)		224 (32,500)
1. Vapor degrease	31 (4500)	38 (5500)	235 (34,100)
2. Cathodic alkaline clean			
3. Immersion in 45 g/l ammonium bifluoride, 3 min at 22 C			
4. Nickel plate	6 (800)	12 (1700)	180 (27,500)

(a) Each reported value is the average of at least two tests. Nickel plating details are outlined in Table I.

(b) A TZM molybdenum ring was used to constrain the specimens during heating. Clearance between the specimens and ring was 25 μm or less on the diameter.

C. Mechanical Treatments

Mechanical treatments such as threading or knurling were also evaluated and these produced good bond strengths (Table V). This is not surprising inasmuch as these machining operations provide regions for "fingering" or interlocking of the plating as shown in Figure 3. Typically, 20 threads 0.13 mm deep were machined per centimeter. Specimens were cleaned, pickled in HCl, and then overplated with chromium, silver, nickel, or electroless nickel coatings. The highest strengths (255 MN/m²) were obtained with the chromium overplates. The values for silver and nickel were not reduced much (184 and 199 MN/m², respectively). Electroless nickel showed the lowest strength (122 MN/m²). Increasing the depth of the threads from 0.13 to 0.26 mm prior to plating with nickel resulted in an improvement in bond strength as expected--269 vs 199 MN/m². The reason for this is that the knurl depth was only about 0.025 to 0.050 mm deep compared to a depth of 0.13 mm for the threaded specimens. Heating knurled or threaded specimens after plating for 2 hours at 700 C in an unconstrained condition did not improve the bond strengths.

TABLE V
RING SHEAR DATA FOR MECHANICAL PREPARATION
TREATMENTS FOR ZIRCALOY-2

(Each value is the average of at least three tests. Specimens were overplated with nickel per the conditions listed in Table I.)

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
"	Same as above, but plated with silver	184	26,700
"	Same as above, but plated with nickel	199	28,800
"	Same as above, but threads were 0.26 mm (20 mils) deep	269	39,000
"	Same as above, but plated with chromium	255	37,000
Knurled Surface	Knurled surface machined on rod, then plated with nickel	115	16,700

Figure 3. Cross Section of a Zircaloy Rod Machined With 20 Threads/cm, 0.13 mm Deep, Overplated With Thin Chromium and Thick Nickel, and Then Tested

Summary

A number of treatments for preparing Zircaloy-2 for plating were quantitatively evaluated by ring shear tests. When chemical activation was used, best results were obtained when the Zircaloy-2 was etched in ammonium bifluoride solution prior to nickel plating. However, even with this treatment, low and inconsistent strengths were obtained. Use of other procedures recommended in the literature gave even poorer results. A noticeable improvement in bond strength was obtained when specimens which had been etched in ammonium bifluoride or ammonium bifluoride/sulfuric acid were heated in a constrained condition at 700 C for 1 hour after plating. Another successful procedure consisted of threading the zirconium prior to plating. However, it is unlikely that the bonds formed by this treatment were anything other than mechanical in nature.

Based on the work described in this paper, it is concluded that Zircaloy-2 could be successfully and reliably joined to other metals by using either an ammonium bifluoride/sulfuric acid or ammonium bifluoride etch prior to nickel plating and then heating at 700 C for 1 hour, preferably in a constrained condition. Suitable adherence for some applications could be obtained by threading or knurling the surface of the Zircaloy-2 prior to plating.

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