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PLATING ON STAINLESS STEEL ALLOYS

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ABSTRACT

Quantitative adhesion data are presented for a variety of electroplated stainless steel type alloys. Results show that excellent adhesion can be obtained by using a Wood's nickel strike or a sulfamate nickel strike prior to final plating. Specimens plated after Wood's nickel striking failed in the deposit rather than at the interface between the substrate and the coating. Flyer plate quantitative tests showed that use of anodic treatment in sulfuric acid prior to Wood's nickel striking even further improved adhesion. In contrast activation of stainless steels by immersion or cathodic treatment in hydrochloric acid resulted in very reduced bond strengths with failure always occurring at the interface between the coating and substrate.

INTRODUCTION

At the last symposium on Plating on Difficult to Plate Metals, sponsored by the American Electroplaters' Society, much interest was expressed in preparing stainless steels for plating but very little coverage was provided on this topic. Although stainless steels have been plated upon successfully for many years, they do require special activating steps to insure adequate coating adhesion and, as such, rightly fall under the category of difficult to plate metals. The purpose of this paper is to gather together some quantitative information that we've obtained on this topic in recent years. A summary of the substrates and electrodeposited coatings that have been evaluated are shown in Table 1. In this paper we will discuss the more important observations gleaned from the work presented in Table 1.

TABLE 1

Stainless Steels and Related Alloys for Which Quantitative Plating Adherence Data are Available

Substrate	Electrodeposited Coating	Test Method	Reference
303,304,321,410,430Ti, 21-6-9, and AM363	Gold	Ring Shear(A)	1,2
405,410,416	Nickel	Ring Shear	3,12
AM363	Nickel	Ring Shear	1,4
AM363,A286,303Se	Nickel-Cobalt	Ring Shear	5
303Se	Copper, Nickel	Ring Shear	5
17-4PH	Nickel	Ring Shear	3
Maraging Steel	Nickel-Cobalt	Ring Shear	5
SA106	Nickel	Ring Shear	3
AM363	Copper	Conical Head(A)	4
AM363,21-6-9,A286	Nickel, Nickel-Cobalt, Copper	Flyer Plate(B)	5
A286	Nickel, Copper	Flyer Plate	6

(A)For complete details on this test see Reference 9.

(B)For complete details on this test see Reference 4.

The surface of stainless steels is unusual in that it is normally resistant to a wide variety of corrosive elements. This property has been attributed to the presence of a thin, transparent oxide film of chromium and/or nickel which quickly reappears after it has been stripped off or penetrated. This film not only protects the metal against attack by corrosive agents, but also prevents the adhesion of electrodeposits. However, once this film is removed and kept from reforming until the surface has been covered with an electrodeposit, any of the common metals may be electrodeposited successfully on stainless steels.

Many procedures have been recommended for activating stainless steels for plating [7]. They include immersion in acids, simultaneous activation-plating treatments such as the Wood's nickel strike[8], anodic treatment in various solutions, and a combination of anodic, then cathodic treatment in highly acidified solutions. The most common method used today is probably the Wood's nickel strike. With this technique, an adherent thin deposit of nickel is applied to the stainless steel substrate and this then serves as a base for subsequent coatings. The Wood's strike contains about 240 g/l nickel chloride and 125 ml/l hydrochloric acid (37% wgt) and is operated with nickel anodes.

EXPERIMENTAL DETAILS

Ring shear and flyer plate tests were used to assess the bond strength of coatings applied to various stainless steels. The ring shear test, which provides quantitative data on bond strength, has been described in detail elsewhere so will only be briefly mentioned here[9]. For this test, a cylindrical rod is coated with separate machined, electrodeposited rings of predetermined width. The rod is then 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 the coating. The area of the test specimen and the load required to cause failure are the data on which strength calculations are based.

The flyer plate test, originally developed for shock testing of materials, consists of utilizing magnetic repulsion to accelerate thin, flat flyer plates against the substrate under test. The flyer travels at speeds around 0.07 cm/μ sec (1550 mph) and induces a compressive wave in the specimen due to impact. As this compressive wave reaches the rear surface of the sample, it is reflected as a tensile wave which propagates back through the specimen. This tensile wave, combined with rarefraction waves from the impedance mismatch at the interface between the substrate and the coating subjects the substrate-coating interface to dynamic tensile stresses. Damage at the interface can then be assessed by visual and metallographic inspection. Details on this test are included in Reference 4.

RESULTS

A. Comparison of Wood's Nickel Strike with Other Activating Treatments

The first item that will be addressed is activation of stainless steel by immersion or cathodic treatment in hydrochloric acid since it has been reported that stainless steel can be activated by either of these simple steps[7]. Ring shear tests with 410 stainless steel revealed that in all cases where these treatments were used, intermediate adhesion was the result and failure consistently occurred at the electrodeposit/substrate interface. Activation of 410 stainless steel by simple immersion in HCl resulted in extremely poor adhesion (5 MN/m^2, Table 2). The best results were obtained with cathodic treatment in hydrochloric acid, but even these bond strengths were still less than one-half as strong as those obtained when a Wood's nickel strike was used (Table 2).

TABLE 2

Influence of Various Activation Treatments on Ring Shear Adhesion of Gold Plated 410 Stainless Steel[(A)]

Treatment	Shear Strength MN/m^2	Shear Strength psi	Location of Failure
Immersion in 6 percent (by weight) HCl	5	700	Gold-Stainless Steel Interface
Cathodic Treatment in 6 percent (by weight) HCl at $968A/m^2$ for 2 min.	15	2,200	Gold-Stainless Steel Interface
Cathodic Treatment in 37 percent (by weight) HCl at $968A/m^2$ for 2 min.	66	9,600	Gold-Stainless Steel Interface
Cathodic Treatment in Wood's Nickel Strike[(B)] at $108A/m^2$ for 2 min.	152	22,000	Within Gold Deposit

(A) For more detail, see Reference 2. The gold was plated in a citrate solution at $32A/m^2$. Stainless steel 410 contains 11.5 - 13.5 Cr and no Ni.

(B) The Wood's nickel strike solution contained 240 g/l nickel chloride and 120 ml/l HCl.

B. Influence of Wood's Nickel Strike Current Density

The influence of current density in the Wood's nickel strike on subsequent adhesion of gold or nickel deposits on stainless steel is shown in Table 3. When no nickel strike was used, failure occurred at the electrodeposit/substrate interface at very low strengths (5 MN/m^2). When the nickel strike was used and overplated with gold, optimum adhesion was obtained when the current density in the Wood's nickel solution was 108 A/m^2, or higher. Prior to nickel sulfmate plating higher, Wood's strike current densities were needed. Fairly strong bonds were obtained with Wood's current densities of 290 and 538 A/m^2, but maximum strengths were not obtained unless the current density in the Wood's nickel strike was 1076 A/m^2, or higher. The fact that a higher current density was required prior to nickel plating than prior to deposition of gold is attributed to the different strength levels of nickel and gold electrodeposits. The higher strength deposit (nickel) was simply more discriminating in terms of proper activation of the substrate.

C. Sulfuric Acid Treatment Prior to Wood's Nickel Striking

The work discussed, thus far clearly shows that when used properly, the Wood's nickel strike provides a bond between stainless steel substrates and subsequent electrodeposits that is at least as strong as the weakest material involved in the process. Another way of saying this is that failure does not occur at the interface between the plating and substrate but within either the electrodeposit or substrate depending on which has the lowest strength. Seegmiller has suggested that a combination of anodic treatment in sulfuric acid followed by cathodic treatment in a Wood's strike may be necessary for insuring a high degree of adhesion[10]. Table 4 shows the benefit of using an anodic treatment in sulfuric acid solution prior to Wood's nickel striking when preparing 17-4 PH stainless steel for plating. The ring shear strength of samples given only a Wood's nickel strike was 195 MN/m^2, whereas, a combination of anodic treatment in sulfuric acid followed by a Wood's nickel strike provided strengths of 472 MN/m^2. This is an unusual result since for

TABLE 3

Influence of Wood's Nickel Strike Current Density on Ring Shear Adhesion of Gold or Nickel Plated AM363(A),(B)

Wood's Nickel Strike Current Density		Ring Shear Bond Strength			
		Gold		Nickel	
A/m^2	ASF	MN/m^2	psi	MN/m^2	psi
0	0	5	700	5	700
54	5	54	7,800	48	6,900
108	10	152	22,000	48	7,000
161	15	152	22,000	54	7,800
291	27	152	22,000	318	46,100
538	50	152	22,000	337	48,900
1080	100	152	22,000	488	70,700

(A) The cleaning/plating cycle consisted of anodic treatment at 323 A/m^2 in hot alkaline cleaner, rinsing, immersion in 18% (wgt) HCl for 2 minutes, rinsing, Wood's nickel striking (240 g/l nickel chloride, 120 ml/l HCl) for 2 minutes, rinsing, and plating in either citrate gold solution at 32 A/m^2 or nickel sulfamate solution at 269 A/m^2. AM363 stainless steel contains 11.5 Cr, 4.5 Ni, 0.50 Ti, 0.04 C, 0.50 Mn, 0.035, 1.0 Si and balance Fe.

(B) For more details see Reference 1.

TABLE 4

Ring Shear Data for Nickel Plated 17-4 PH Stainless Steel[A],[B]

Cleaning/Activating Cycle	Ring Shear Strength (MN/m^2)	(psi)
Clean[C], HCl Pickle, Wood's Nickel Strike at 268 A/m^2 for 5 min., Sulfamate Nickel Plate	195	28,200
Clean, HCl Pickle, Anodic Treat in 70 wt. % H_2SO_4 at 1070 A/m^2 for 3 min., Wood's Nickel Strike at 268 A/m^2 for 5 min., Sulfamate Nickel Plate	472	68,300

(A) The composition (in wt. %) of 17-4 PH stainless steel is 0.04 Carbon, 0.40 Manganese, 0.50 Silicon, 16.5 Chromium, 4.25 Nickel, 0.25 Iridium, 3.6 Copper and the remainder is Iron.

(B) For more details see Reference 3.

(C) In all cases the cleaning step included degreasing, then anodic and cathodic treatment in hot alkaline cleaner. The HCl pickle was 30 wt. %.

most stainless steels, the ring shear test does not provide discrimination between Wood's nickel and anodic sulfuric acid treatment since failure typically occurs in the nickel deposit regardless of which procedure is used. For example, when AM363 stainless steel was plated with either nickel or nickel-cobalt, ring shear adhesion tests showed no difference between Wood's strike activation and activation in anodic sulfuric acid followed by Wood's strike since all failures occurred within the electrodeposited coatings. By contrast, flyer plate tests showed approximately a 50% improvement in bond strength when the sulfuric acid treatment was used prior to Wood's striking (Table 5).

TABLE 5

Influence on Static and Dynamic Adhesion of Anodic Treatment in Sulfuric Acid Prior to Wood's Nickel Striking of AM363 Stainless Steel[A],[B]

Activation Treatment	Electrodeposit	Dynamic Adhesion (Flyer Plate Spall[C] Threshold Velocity), MN/m^2	Dynamic Adhesion, psi	Static Adhesion (Ring Shear Strength), MN/m^2	Static Adhesion, psi
Wood's Strike	Nickel	4000	579,000	455	66,000
Anodic Sulfuric Plus Wood's Strike	Nickel	6000	868,000	455	66,000
Wood's Strike	Nickel-Cobalt	4480	648,000	559	81,000
Anodic Sulfuric Plus Wood's Strike	Nickel-Cobalt	6700	969,000	559	81,000

(A) Spall is the separation of the plated deposit from the substrate due to the interaction of two rarefraction waves.

(B) For more details see Reference 4.

(C) The complete preparation cycle included anodic cleaning in hot alkaline solution, rinsing, immersing in 18% (wgt) HCl at room temperature for one minute, rinsing, anodic treating in 70% (wgt) sulfuric acid at 1080 A/m^2 (100 A/ft^2) for 3 minutes, rinsing, and then Wood's striking at 270 A/m^2 (25 A/ft^2) for 5 minutes prior to nickel or nickel-cobalt plating in sulfamate solution. In some cases, the anodic treatment in sulfuric acid was omitted as indicated above.

D. Sulfamate Nickel Strike for 405 Stainless Steel and Nickel

Often the electroplater is confronted with the problem of activating stainless steel in the presence of other metals which may be attacked by the chloride ions in the Wood's nickel strike solution. Such was the case in Reference 11 where 405 stainless steel and nickel had to be simultaneously activated in the presence of bare aluminum and then overplated with nickel. Adherence to the aluminum was not required as it was a mandrel in the electroforming process and was subsequently dissolved. To overcome the objection of the chloride ion, a sulfamate nickel strike was developed which gave excellent adhesion to both the 405 stainless steel and nickel without attacking the aluminum. The nickel strike composition was 80 g/ℓ nickel (as nickel sulfamate) and 150 g/ℓ sulfamic acid and was used at 50^{o}C with electroformed nickel sheets as anodes. An anodic/cathodic treatment in this solution was found to be the optimum with failure occurring in the stainless steel and not at the plating interface. Similar results were obtained where the nickel was activated with the sulfamate strike with failure occurring in the original nickel. Ring shear data for this work is shown in Table 6.

SUMMARY

Quantitative test data verified that excellent adhesion can be obtained on a variety of stainless steels by using the Wood's nickel strike. Ring shear test specimens of stainless steel plated with either gold or nickel after Wood's nickel striking failed in the deposit rather than at the interface between the substrate and coating and bond strength was directly related to current density once a minimum current density had been obtained. Use of anodic treatment in sulfuric acid prior to Wood's nickel striking further improved adhesion as shown by dynamic flyer plate tests. By contrast, activation of stainless steel by immersion or cathodic treatment in hydrochloric acid resulted in very reduced bond strengths with failure always occurring at the interface between the coating and substrate. In cases where the chloride ions in the Wood's strike could be detrimental to portions of a composite substrate containing stainless steel, nickel and aluminum, a sulfamate nickel strike was shown to provide excellent adhesion.

TABLE 6

Ring Shear Data for
Nickel-Plated 405 Stainless Steel

Code	Cleaning/Activating Cycle	Ring Shear Strength[A] MN/m^2	(psi)
1	Clean, pickle, sulfamate nickel strike at 108 A/m^2 - 5 min. nickel plate	345	50,000
2	Clean, pickle, sulfamate nickel strike at 270 A/m^2 - 5 min. nickel plate	338	49,000
3	Clean, sulfamate nickel strike at 108 A/m^2 - 5 min. nickel plate	221	32,000
4	Clean, sulfamate nickel strike, 270 A/m^2 - 5 min. nickel plate	373	54,000
5	Clean, sulfamate nickel strike anodic at 540 A/m^2 - 1 min., the cathodic at 540 A/m^2 - 5 min. nickel plate	428	62,000
6	Same as 5, but heated at 200°C for 16 hrs. before testing at room temperature	428	62,000

(a) All reported values are the average of at least two tests.

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