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EFFECTIVENESS OF NICKEL PLATING IN INHIBITING ATMOSPHERIC CORROSION OF COPPER ALLOY CONTACTS

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ABSTRACT

A series of tests was run to determine the effect of Ni plating thickness on connector contact resistance. Copper coupons were plated with an electrolytic nickel strike followed by electroless nickel to produce Ni layers of 10, 20, 55 and 100 μin . The coupons were then exposed to a simulated industrial environment. Pore corrosion was observed after the exposure, which correlated with Ni thickness. In a second series of tests, beryllium-copper four-tine contacts with 50 μin of gold plate over electrolytic nickel strike/electroless-nickel plates of varying thickness were exposed the same corrosive environment. Contact resistance of mated pairs was monitored over a two-month period. The degradation in contact resistance correlated with the Ni thickness used in the connectors.

Keywords: Contact resistance, nickel underplate, gold plate, nickel porosity, corrosion resistance.

INTRODUCTION

Connectors in nuclear weapons must exhibit a low and stable contact resistance over the life of the system. Current life requirements exceed 20 years. Examples of connectors used in weapon systems are high voltage (HV), radio frequency (RF), lightning arrestor connectors (LAC), circular hermetic, and rack and panel (R&P) types. Typical contacts in these connectors use a beryllium-copper alloy for the spring member. Electrodeposited coatings are used to provide corrosion protection and to enhance the physical and electrical properties of the copper alloy contacts. Typically, these coatings are relatively thick gold over nickel (1) although contacts using a gold flash over palladium or palladium-nickel alloys have seen increased usage (2). The nickel provides a diffusion barrier between the gold and the underlying copper alloy substrate (3). The nickel also improves the hardness and wear resistance of the contact and reduces the effect of porosity in the gold overplate (4). The gold layer provides good electrical conductivity with long term stability in corrosive atmospheres.

Corrosion of the base material through pores in the plating is one mechanism by which the contact surface is degraded. Pore corrosion occurs when atmospheric pollutants react with the base metal through pores in the plated layer. The corrosion products creep across the contact surface and form an insulating layer that increases contact resistance.

Porosity of plating is dependent on plating thickness, substrate surface (roughness and defects), plating solution contaminants, and the type of plating used. Electroless plating and pulse plating reduce pore densities for many materials (5). Plating porosity can also be influenced by the nature of the underplate used between the top plating and the substrate (6).

Other factors affecting contact resistance of gold over nickel systems include the amount and type of hardeners used in hard gold plating (7). At temperatures above 150 C, the contact resistance of gold over nickel increases as the amount of cobalt and nickel hardeners in the gold increase.

Our objective in this study was to determine the lower thickness of nickel that would effectively inhibit corrosion of the beryllium-copper contact. The driver for this study was to relax potentially conservative specifications for plating contacts used in connectors. Adhering to overly conservative plating specifications ultimately adds cost to the finished connector, not only from the additional raw materials, but also from scrap and rework incurred by non-conformance.

The performance of each nickel thickness was determined by measuring the extent of pore corrosion on copper test coupons and by measuring contact resistance of a four-tine, double-ended contact design currently used in the production of circular hermetic connectors. Electroless nickel was chosen because it is a common coating used in the construction of many of our connector contacts.

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EXPERIMENTAL

The plan for evaluating nickel plating was divided into two tasks. The first was to determine the porosity of the nickel plating on flat copper test coupons. This established the properties of the nickel plate itself. The second task was to determine if contacts employing different thicknesses of nickel overplated with 50 μin of Au showed differences in corrosion rate and contact resistance when aged in a Battelle Class II flowing mixed gas (FMG) environment.

Porosity

Plating coupons were prepared from 0.032" thick, copper alloy 101 (oxygen-free, high conductivity-OFHC) sheets. Each 6" by 11" sheet contained sixty, 0.75" x 1" coupons that had been cut in a matrix leaving small tabs on each side of the coupon. These tabs held the coupons during plating and were cut to remove the coupons for testing. After machining the coupon matrix, the copper panels were wire brushed. Surface finish of the bare panels after brushing ranged between 19 and 32 μin RMS as determined by contact profilometry.

The matrix of coupons was plated as a panel to improve uniformity in plating thickness. Standard surface preparation of the panels was performed before plating with proprietary plating solutions. Each panel was plated with a Woods nickel strike followed by electroless nickel (EN) to the final desired thickness.

We attempted to quantify the porosity of the nickel-plated copper coupons using three different techniques: the standard ferroxyl test (ASTM B689) modified for use with copper substrates (8,9) and exposure to the Battelle Class II FMG atmosphere followed by optical pore counting or elemental mapping using scanning electron microscopy (SEM) in the energy dispersive X-ray mode (EDX). The ferroxyl test involves preferentially corroding exposed copper from the substrate and complexing it with an agent to render it visible. The exposure is performed using reagent-filled filter paper. After exposure, the filter paper is examined for blue corrosion products formed from the association of copper with the ferricyanide in the filter paper.

To determine the relationship between porosity and thickness, the vendor plated four coupon sheets with nominal nickel thicknesses of 10, 20, 55, and 100 μin . All sheets had an initial Woods nickel strike of approximately 10 μin . The 20, 55, and 100 μin panels had the balance of plating thickness made up with electroless nickel.

Plating thickness was verified by measuring both sides of 16 coupons from each sheet using XRF (X-ray fluorescence). Coupons were selected along a 'Z' pattern to determine plating variability across the sheet. The results of these measurements are shown in Table A. As a comparison, the plating of one coupon was also measured by optical metallography. The

results, shown in Table B, illustrate good agreement between the measurement techniques.

Table A. Nickel Thickness on Coupons by XRF

Specified Thickness, μin	Average Thickness, μin	Standard Deviation, μin
10	16	3.5
20	26	2.7
55	59	2.2
100	90	3.6

Table B. Comparison of XRF Thickness with Optical Cross-Section

Specified Thickness, μin	XRF (10 point average)	Optical Metallography (50+ points)
10	13.8	14.3
20	24.0	21.3
55	57.4	62.0
100	87.0	90.3

Five samples from each thickness group were exposed to a Battelle Class II FMG atmosphere for 34 days (10,11). The Class II environment contains 10 ppb H_2S , 10 ppb Cl_2 , and 200 ppb NO_2 at 30C and 70% RH. It is designed to be an accelerated atmospheric corrosion test that is relevant to indoor industrial exposures. The pollutant gases are supplied by permeation tubes, mixed with dry laboratory air and introduced into an exposure chamber. The coupons were photographed prior to exposure to establish a surface baseline and again after exposure to document the porosity.

Contact Resistance

Size 20 (.040" pin diameter) socket contacts used in the manufacture of circular hermetic connectors were used to make contact resistance measurements. A photograph of a single contact is shown in Fig. 1. These contacts are a double-ended, four-tine design fabricated from beryllium-copper, alloy 25 (ASTM-B 196). A stainless steel sleeve covers the tine portion of the contact. Nominal contact load for this design is 100 g.

Figure 1. Individual four-tine contact with protective sleeve.

To discern the effect of nickel thickness, 3 groups of contacts were plated with approximately 25, 100 and 200 μin of electroless nickel followed by approximately 50 μin of gold. Ni was a hardener in the 99.7% pure gold plating. Actual plating thickness was measured on a sampling from each group and the statistical data is presented in Table C. The location at which the measurements were made was along the contact point of the tines. A control group of unplated contacts was also included in this study.

Table C. Contact Plating Thickness

	25 μin group		100 μin group		200 μin group	
	Ni	Au	Ni	Au	Ni	Au
XRF thickness (8 samples)						
Avg.	26.8	86.6	108.6	80.6	195.1	86.5
Max	33.0	94.2	121.5	88.9	209.4	97.6
Min	20.8	73.9	103.8	73.3	180	72.1
St. dev.	4.14	7.8	5.72	6.7	9.02	8.1
Optical cross-section thickness(5 samples)						
Avg.	39.0	109.6	111.0	114.9	185.9	113.3
Max	64.0	165.8	152.7	142.1	265.3	211.4
Min	21.1	37.9	91.6	39.9	143.3	59.8
St. dev.	10.0	23.7	9.9	11.4	28.8	17.5

Rectangular rack and panel connectors with 24 size 20 pin contacts in a standard density insert arrangement were used as mating fixtures for the four-tine socket contacts. A photograph of a connector and the socket contacts is shown in Fig. 2. The connector contacts were plated with 50 μin of gold over 100 μin of nickel.

Figure 2. Rectangular connector used for this study. Individual socket contacts that were mated to the connector are shown above.

Contact resistance of the connector and socket pair was measured with a Keithley model 580 micro-ohm meter using a Keithley Model 7002 switch system to scan the contact pairs. A dry-circuit setting of 20mV and 10mA was used. The source and sense leads of each channel were soldered directly to the solder cup of the rack and panel connector as well as to one end of the socket contact that had the protective sleeve removed.

Twenty-four socket contacts from each of the four plating groups were mated to rack and panel connectors and each contact pair was wired to the scanner. The four socket-connector 'fixtures' were aged in Battelle Class II environment and the contact resistance of each contact was measured periodically. Twice during the exposure, each contact pair was disturbed by unmating and remating at 34 and 70 days exposure.

Additionally, 10 samples from each group were exposed in an unmated condition to determine if corrosion in the bottom of the socket bore would occur. These were loose socket contacts that were not wired for contact resistance measurements.

RESULTS

Porosity

For even the thinnest nickel deposits, very little coloration was observed on the filter paper from the ferroxy tests with the naked eye. Even after optical magnification to 10x, only a few blue colorations were visible. Pore densities using the ferroxy test, evaluated at a magnification of 10x, are shown in Table D.

Optical pore counting was performed on coupons that had been exposed to the Class II atmosphere for 34 days. Optical pore counts were determined by photographing the coupons

and digitally enhancing the images to highlight pores. Pores appear as dark spots on the image due to corrosion products of copper and sulfur and/or chloride on the surface of the nickel plate as shown in Fig. 3. Pore counting was performed at 10x and 40x. At 10x, the imaged area reflected about 10% of the total area of the sample. Pore densities using this technique are shown in Table D.

Figure 3. Optical micrograph of the nominal 10 µm Ni sample after exposure to Class II environment.

Table D. Pore Densities by Ferroxy Test and Optical Counting after Class II Exposure.

Nominal Ni Thickness, µin	Ferroxyl Pore Density (#/cm ²) at 10X	Optical Pore Density (#/cm ²) at 10X and 40X	
10	1	730	1140
20	0	27	ND*
55	0	5.7	ND
100	0	1.9	ND

*ND = not determined.

Because the pore densities were so low on the 3 thicker nickel samples, pore densities were not determined at 40x. The results indicate that, as expected, pore density decreases with increasing thickness. Much of the difference in pore counts between the thinnest nickel plate (electrolytic Woods strike) and the other samples with electroless Ni could be due to deposit morphology.

The presence of pores in the plated Ni layer can lead to corrosion of the underlying Cu substrate. To verify that corrosion is, in fact, taking place, electron microprobe analysis of the coupon surfaces was performed. Fig. 4 shows results for a copper coupon covered with 20 µin of Ni. The first two images show the SEM and backscattered (BSE) images of the surface. Surface roughness is evident in these images. In addition, the BSE image exhibits dark spots that cannot be attributed to surface topography. The following images are elemental maps that can be used to determine the composition of the dark spots. In these images, brightness correlates with concentration. Fig. 4(c) shows the Ni map for the surface. The surface is primarily Ni, with several dark spots indicating the presence of another element. Correlation with (d), (e), and (f)

shows that the dark areas are due to the presence of copper corrosion products containing Cu, S, and Cl. The correlation between the Cu map and the S and Cl maps clearly indicates that Cu migrated through pores in the plated Ni layer and underwent corrosion upon exposure to the Class II environment.

Figure 4. Scanning electron microscope (SEM) images (a), back-scattered electron (BSE) images (b) and elemental maps (c-f) of Ni-plated (20 µin) Cu coupon exposed to class II environment. The bright spots indicate the presence of the specific element.

Similar results are shown for the 10 µin Ni sample in Fig. 5. The BSE image clearly exhibits large areas of copper corrosion. The elemental maps show that the corrosion products have spread with time. As with Fig. 4, the corrosion products are Cu salts containing S and Cl. For the 10 µin sample, it is clear that the pores are larger and more numerous. The extent of corrosion is such that connectors under similar conditions might be expected to exhibit unacceptable values of contact resistance. Additionally, there is nothing to suggest that the corrosion process has proceeded to termination. The corrosion products will continue to spread and thicken as they are exposed to a corrosive environment.

Figure 5. Back-scattered electron microscope image (a) and elemental maps (b-d) of Ni-plated (10 μ in) Cu coupon exposed to class II environment. The bright spots indicate the presence of the specific element.

Quantitative line scans were also run on the surface of the corroded coupons. Results are shown in Fig. 6 and 7 for the 20 and 10 μ in samples, respectively. In both cases, the pores are readily apparent through the decrease in the Ni concentration and the increase in Cu, S, and Cl. The pores seen on the 20 μ in sample were quite small ($\sim 10 \mu$ m) and are filled with Cu corrosion products. The pores on the 10 μ in sample were much larger (30 – 50 μ m) and the Cu concentration in the pore was higher. The halo (observed in the BSE image) can also be seen as a shoulder of intermediate Cu concentration.

Figure 6. Line scan of Ni-plated Cu substrate (20 μ in Ni) exposed to Class II environment. Note that the Cu, S, and Cl increase where the Ni decreases, indicating the presence of pores in the Ni.

Figure 7. Line scan of Ni-plated Cu substrate (10 μ in Ni) exposed to Class II environment. Note that the Cu, S, and Cl increase where the Ni decreases, indicating the presence of pores in the Ni.

Contact Resistance

The contact resistance of the aged mated contacts was plotted using a cumulative distribution scale. The value of presenting resistance data in this manner is that normal distributions are easily recognized as straight lines. A normal distribution indicates that the conduction mechanism is metallic and stable. Deviation from a straight-line plot in the form of high resistance values or 'tails' means that the distribution is no longer normal and is an indication that the contact has degraded. In this study, the degradation of the contact is due to corrosion.

The amount of degradation can be equated to the percentage of contacts that have deviated from the straight line and reside in the high resistance tail portion of the plot. Also, it is the change in resistance and not the magnitude of the resistance that is significant. A customary failure criterion is a change in resistance of 5 to 10 m Ω . A resistance change of this magnitude indicates that the contact has degraded and is no longer stable.

The initial contact resistance measurements of the four populations are shown in Fig. 8. Two observations are apparent. As expected, the magnitude of the resistance for all contacts is only a few m Ω and the resistance of the bare contacts shows a tendency toward being non-normal. Being unprotected, the bare contacts had already formed surface oxides prior to being mounted to the fixtures and tested.

Figure 8. Contact resistance prior to atmospheric exposure.

Fig. 9 and 10 are plots of contact resistance after 34 days of exposure for the undisturbed and disturbed conditions respectively. The contact resistance for the unplated contacts has increased from the initial condition and also show further deviation from a normal distribution.

Figure 9. Contact resistance after 34 days of exposure to Class II environment. Note the deviation from linearity in the no plate condition, indicating degradation in contact reliability.

Figure 10. Contact resistance after 34 days of exposure to Class II environment. Connectors were disturbed prior to resistance testing.

After disturbing the contacts, an increase in resistance is observed for both the unplated and the thinnest plated (40 μin) populations. Although this increase is only a few $\text{m}\Omega$, the trend suggests that these two populations are unstable. The 110 and 190 μin populations, by comparison, remain unchanged.

Contact resistance of the four populations after aging of an additional 36 days is shown in Fig. 11 and 12. The continuing degradation of the unplated population is evident as shown by the significant portion of the population residing in the high resistance tail of the distribution. Although not as severe, the 40 μin population show similar behavior, especially after being disturbed. Although the additional exposure time has not dramatically affected the contact resistance of the unplated and 40 μin populations, there appears to be a trend toward increasing contact resistance with exposure. By contrast, there is virtually no change in contact resistance for either the 110 μin or 190 μin populations.

The 10 samples that were exposed in an unmated condition for 34 days were optically examined. No corrosion was observed in the bore or at the bottom of the contact.

Figure 11. Contact resistance after 70 days of exposure to Class II environment

Figure 12. Contact resistance after 70 days of exposure to Class II environment. Connectors were disturbed prior to resistance measurement.

CONCLUSIONS

The evaluation of pore density of the nickel deposits on the copper coupons showed the expected trend of decreasing density with increasing deposit thickness. For deposits thicker than about 50 μin , little further improvement in pore density was demonstrated with increasing thickness. Pores were identified both optically and by elemental analysis. Elemental analysis showed that corrosion products at the pores were formed from Cu, S, and Cl.

The corrosion protection afforded by each thickness of nickel plating is apparent from the plots of contact resistance measurements. Although the sampling was small (24 data points per population), a trend was observed in the contact resistance distributions between the thinner and thicker-plated

populations. Both the no-plate and 40 μin groups showed degradation in contact resistance during exposure while the 110 and 190 μin groups appeared unaffected by the exposure. While it is unclear what minimum thickness of nickel would still provide adequate corrosion protection, it appears that a nickel thickness of 100 μin would be sufficient to provide long term stability of the contact.

Of course, this study was limited to a single plating vendor and it would be necessary to include others in order to make a more complete statement since the plating process itself is a major variable in determining the porosity/thickness relationship.

It is interesting to note that the actual resistance changes for both the 40 μin and no-plate populations are rather small. One might expect a larger increase in resistance considering the duration of exposure. The small increases in resistance are likely due to the design of the contact. The four-times provide multiple contact points and tend to equalize the contact load. Also, the sleeve shields the sensitive portion of the contact reducing exposure to the corrosive environment. Had contacts been exposed to the test atmosphere in an unmated condition, degradation of the contacts could have occurred sooner and been more severe.

Further tests of nickel plating in the 50-100 μin thickness range as well as the addition of other plating vendors to the study are recommended to completely characterize the minimum nickel thickness necessary to ensure long-term stability of these contacts.

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