

A Comparison Study Focused on the use of Electroplated Zinc Material as an Alternative to Electroplated Copper Material

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Abstract

Manufacturers of electronic components continually search for more cost effective solutions to the escalating price of raw materials, innovative alternatives for base metals are being explored. One of the proposed base materials being considered is zinc and zinc alloys. As this abstract is being written the cost of copper is approximately three to four times the cost of zinc. Limitations for direct replacement include differences in certain physical properties such as tensile strength, hardness, and toughness. Some of these properties can be replicated by increasing material thickness or adding alloying elements to overcome limitations. This paper will focus on other limitations found in zinc such as contact resistance, solderability, and surface corrosion (white rust). By applying certain electroplated coatings to the zinc base material, many of these surface related restrictions can be overcome. This paper will compare electroplated zinc coupons to similarly electroplated copper coupons. These samples will be exposed to both thermal and thermal/humidity test conditions in an effort to replicate aging effects. Once aged, the test coupons will be tested for solderability and contact resistance. Cross-sectional analysis will be utilized in an effort to analyze the effects of temperature on the migration of the base material. Several types and thicknesses of barrier layers will be utilized to develop a system that is resistant to the effects of zinc migration.

Keywords: electroplating, zinc, material

Introduction

Alternative materials are constantly being considered, as the price of base materials increase. Electronic component manufacturers are some of the most cost competitive businesses in the world. In an industry where costs are continually being reviewed, manufacturers are open to any and all ideas if the outcome is to cut cost while maintaining or increasing the quality of their product.

In an article from Purchasing Magazine Patrick Scholler, Procurement Director for Hewlett Packard, states "Our margins are thin and any variation in the material cost can have a dramatic impact on a given business unit." It has such an impact because material costs can be about 75 – 85% of the overall cost of an HP computer.^[1] Based on Scholler's comments price fluctuations as well as raw material costs are areas of concern.

Currently, copper and copper alloys are a mainstay for both the connector and the lead frame manufacturing industry. Over the past 5 years, copper has increased in cost over 350%. With copper

approaching the four dollar a pound mark electronics manufacturers are looking for cost competitive alternatives. This paper will focus on the use of zinc as a possible alternative for copper in certain applications. Zinc was chosen for its economical benefits when compared to copper. Comparatively speaking, zinc metal prices are about 25% that of pure copper base material.

Much of the work to date with respect to the use of zinc in place of copper has focused on flat blade connectors. Flat blade connectors in large part are a relatively simple type of connector device. Flat blade connectors can be found extensively in automotive applications such as fuses, switches and sensors. Due to its uncomplicated design, flat blade connectors appeared to be the best place to test the theory that zinc and zinc alloys could be used as an alternative for copper and copper alloys.

At the start of this study it became quite apparent that zinc, without a modified surface layer, would not be a viable connector substrate. Zinc could, in certain applications, be used as a substrate,

but due to its inherent oxidizing nature would have to be modified to provide the necessary electrical properties as well as ensure long term stability of those electrical properties.

To counteract this zinc oxide potential, several electroplated layering systems were tested in an effort to stabilize the surface of the zinc material in order to provide the necessary electrical properties. The following study tests the viability of the proposed coated layering systems and exposes these coatings to environmental conditions designed to replicate long term exposure conditions.

Test Matrix

Most flat blade connectors produced today are electroplated on continuous reel-to-reel plating equipment. Therefore, test coupons for this study were gathered from samples produced on continuous reel-to-reel plating equipment. For this study all of the samples incorporated a core consisting of a zinc alloy strip material measuring 0.254 mm (0.010") x 25.4 mm (1.000"). The zinc alloy used in this study is comprised of copper (0.60 wt. %), titanium (0.15 wt. %) and the remainder zinc. This alloy was chosen for its good strength and moderate ductility properties. This alloy can be found in automotive fuses, low voltage electrical terminals and bussbar applications. Subsequent layers of copper, nickel and tin were electroplated onto the zinc. Each test sample group consisted of varying thicknesses and quantities of the above described plating system. Table 1 describes the various barrier layer compositions and thicknesses.

Sample	Base Material	Barrier Material	Barrier Thick. (μ-in.)	Tin Thick. (μ-in.)
1	Zinc	Copper	50	80
2	Zinc	Nickel over Copper	50 Copper, 25 Nickel	80
3	Zinc	Copper	100	80
4	Zinc	Nickel over Copper	100 Copper, 25 Nickel	80
5	Alloy 654	N/A	N/A	80
6	Alloy 425	Copper	25	80

Table 1

Samples numbered 1 through 4 all had two constant factors; they all had the same zinc alloy base material and they all had a top layer of tin plating on the order of 80 micro-inches thick. Table 1 shows that two different metals were used in the barrier layers for samples 1 through 4. Sample 1 had a relatively thin layer of copper as a barrier layer while sample 2 consisted of the thin copper layer capped with a 25 micro-inch layer of nickel. Sample 3 had a relatively thicker layer of copper as a barrier layer while sample 4 consisted of the thick copper layer capped with a 25 micro-inch layer of nickel. Samples 5 and 6 were used as reference samples. These 2 samples are indicative of base material and plating combinations that are currently used in connector applications. Sample 5 has a base consisting of a 654 copper alloy

with no barrier layer and a tin coating equal to that of the zinc samples. Copper alloy 654 is comprised of silicon (3.0 wt. %), tin (1.5 wt. %), chrome (0.4% wt. %) with the remainder copper. Sample 6 has a base material made from a 425 copper alloy with a thin copper barrier layer and a reflowed tin coating equal to that of the zinc samples. Copper alloy 425 is comprised of zinc (9.5 wt. %), tin (2 wt. %) and the remainder copper.

Testing Procedures

Sample coupons were placed in an air-circulating oven and baked at various temperatures for various durations. Sample coupons for each group were pulled and analyzed at bake temperatures equal to; room temperature, 85°C (185°F), 125° (257°F), and 150°C (302°F), and times equal to: 0 (or as-plated), 24 hours, 168 hours and 1,008 hours.

As samples were pulled from the oven they were tested to ensure that the plated layers were still adhered to the base material. Sample coupons were subjected to a bend test where the strip material was bent over on to itself (180° bend). Once bent the coupon had an adhesive tape applied to the bend and pulled away. If any residual plating particles were observed pulling away from the material the part would be labeled as failing the adhesion test.

Once the samples were baked they were subjected to solderability testing. Solderability inspection was conducted per MIL Standard 202F. The test was conducted using a mildly activated flux; samples were visually inspected for solder coverage. Samples exhibiting 95% or better coverage were judged to have "good solderability". This "dip and look" method, which is widely used in process quality assurance and reliability monitoring, is a qualitative test, judgment on whether a sample passes or fails the test is based on the physical and visual attributes that it exhibits.

Samples were also subjected to a wetting balance solderability test. The wetting balance analysis is a quantitative test, it measures the wetting forces imposed by the molten solder on the test surface as it is dipped into and held in the solder bath as a function of time and plotted. The plot starts with the wetting force being negative (non-wet condition), which rises until it crosses the zero axis of wetting force, indicating that wetting has occurred. The time it takes for wetting to occur is one parameter used to assess solderability. There are, however, no established industry-standard pass/fail criteria for wetting balance analysis, for the purpose of this testing we have chosen 1 second as the pass/fail criteria.

Samples were also subjected to contact resistance testing. Contact resistance is evaluated using the practices, outlined in ASTM specifications

667 and 539^{[2][3]}. Method C, Dry Circuit Testing, is used in this study. A power supply which delivers an open circuit voltage of 20 millivolts maximum, with a short circuit current of 100 milliamps is used. It consists of: 1) A programmable servo motor controlled gold probe (for Z axis stroke control), having a radius of 3.2 mm, 2) A sample stage with manual X, Y, Z position control, 3) A Keithley 580 micro-ohm meter which supplies the small open circuit voltage and measures the sample contact resistance, 3) An in-line Omega LCF series tension/compression load cell, and 4) An Omega type 41 controller. Prior to and after each measurement, the contact resistance of a pure gold standard coupon is checked to assure it is within the range 0.75 to 1.5 milliohms at 50 gram load. Three measurements of the gold standard are made before and after test, all of which must be within the specified range for the test data to be valid.

The contact resistance for the candidate alloys is measured as a function of aging time at various temperatures. Exposure times are 0, 24, 168, and 1008 hours. Contact resistance data values at each exposure condition at 100 grams normal load are the reported median of ten random measurements taken along the approximate specimen centerline. The probe is brought into close proximity with the specimen surface, and then as contact is made, the load is increased to the test value of 100 grams. There is a slight relaxation of applied load over the first twenty seconds as the system stabilizes. After stabilization, the test load is slowly increased back to 100 grams, at which point the resistance value is recorded.

Lastly samples were examined via metallographic cross-section. Samples were exposed to the elevated temperatures and then copper backed and mounted into plastic casings using a cold mount system. The cold mount system ensured that plastic encapsulation process did not introduce any external factors to the thermal aging. The molded samples were ground, polished and etched prior to examination at 1,000X magnification. The purpose of the cross-section analysis was to visually capture the physical changes that happen during the diffusion process.

Results

Adhesion test results can be found in Figure 1. All of the test coupons passed the adhesion test in the as-plated condition as well as at room temperature all the way out to 1,008 hours. Samples 3 and 4 were the first samples to fail the adhesion test; both lost adhesion at 85°C for 1,008 hours. Samples 1 and 5 were the next to fail at 125°C at durations of 168 and 1,008 hours, respectively. The two

remaining samples 2 and 6 survived the full 6 weeks at 150°C.

Figure 2 graphically represents the results of the 85°C solderability testing as depicted via the wetting balance solderability test. For the sake of this study we decided to choose 1 second as the pass-fail criteria. Anything with a value of greater than 1 second was considered a failure with respects to solderability. Anything less than 1 second was considered to have passed the solderability test. Samples 3 and 4 were removed from the 85°C solderability testing due to peeling noted in the adhesion test results. Figure 3 depicts the test results for the wetting balance test for coupons subjected to the 125°C temperature. Samples 1, 3, 4 and 5 needed to be removed from this graph due to adhesion issues. Neither sample 2 nor 6 passed the 1 second minimum wetting criteria outlined earlier in the Testing Procedures section.

Contact resistance test results can be seen in Figures 4 and 5. Figure 4 depicts the contact resistance results for the samples exposed to 85°C out to 1,008 hours. While Figure 5 shows similar results for the 125°C baked samples. Samples exhibiting a contact resistance reading of less than 10 milli-ohms were labeled as passing anything over 10 milli-ohms would have failed the contact resistance test. Samples that failed the adhesion test at given temperature were disregarded from that set of contact resistance testing. In the 85°C test group samples 3 and 4 were taken out and in the 125°C group samples 1, 3, 4, and 5 were ignored.

Metallographic cross-sections were prepared for all the baked samples. Special attention was directed toward sample 3 due to the adhesion failure early in the thermal aging test. Photos 1, 2 and 3 depict the metallurgical system of sample 3 at 1,000 X magnification at 85°C for the as-plated, 168 and 1,008 hours (respectively). Sample 2 was given special attention also due to its ability to pass the adhesion test at extended times and temperatures. Photos 4, 5 and 6 depict the metallurgical system of sample 2 at 1,000 X magnification at 85°C for the as-plated, 168 and 1,008 hours, respectively.

Discussion

Adhesion testing proved to be a critical aspect of the plating system after extended exposure to increased temperatures. Certain electroplated layering systems failed the adhesion test at relatively low temperatures. The source of the adhesion defects appears to have been caused by the quick diffusion of the zinc base material into the electroplated copper barrier layer. Further research of this type of defect led us to a paper written by Ernest Kirkendall in the late 1940's. Kirkendall theorized that if interdiffusion between two metals is uneven, since atoms of one

metal may have a higher mobility and diffuse across the junction more rapidly than the atoms of the other metal, this imbalance results in vacancies or voids at the interface between the two metals^[4]. Excess vacancies are left behind in the layer of the faster diffusing element, and these coalesce into a line of porosity known as Kirkendall porosity or voids^[5]. Evidence of this type of void can be seen in photo 3. Inspection of the metallographic cross-sections leads us to believe that all of the zinc electroplated material that failed adhesion testing was due to an overabundance of this voiding occurring between the zinc and the zinc-rich, copper/zinc layer.

Two samples passed the adhesion test after exposure to 125°C for 1,008 hours. Sample 2 electroplated with copper, nickel and tin passed the bake test and performed well with respect to the adhesion test. Further investigation was necessary to understand why this sample passed the adhesion test when other samples didn't. An SEM/EDS line scan was conducted on sample 2 and can be seen in figure 6. As illustrated in figure 6 the nickel layer was quite effective at preventing the zinc from migrating into the tin area and actually alloyed with some of the copper. It appears that this nickel/copper alloy was the reason the zinc was not able to continue its fast diffusion and ultimately hampered the conditions necessary to form the Kirkendall voids. Figure 6 also shows the extent of the copper migration into the zinc substrate. Sample 4 had a metallurgy system similar to sample 2 but had a thicker copper layer. This additional free copper allowed the zinc to consume the copper and complete the void exchange before it reached the nickel/copper alloy which would have slowed the zinc diffusion rate and effectively eliminated the adhesion issue.

Sample 6 also passed the adhesion test. Copper alloy 425 has the reputation as a base material that is well suited for demanding applications and is especially well suited for long term, extended temperature electrical applications.

Samples 2 and 6 were the only combinations that survived the adhesion test and were evaluated further for solderability and contact resistance. Both samples did well in the wetting balance solderability test after exposure to 85°C for 1,008 hours. Neither of the samples met the 1 second solder criteria after exposure to 125°C for 1,008 hours. Both samples 2 and 6 performed well with respect to the contact resistance test after exposure to both the 85°C and 125°C for 1,008 hours.

It should be noted that during the sample preparation stage, samples 1 through 4 were also exposed to a reflow furnace effectively doubling the amount of coupons tested. In every instance the reflowed samples failed in every respect at a slightly

quicker rate when compared to its non-reflowed counterpart. As mentioned previously in this paper, the addition of heat to these plating systems promotes the diffusion of certain metals; primarily the migration of zinc into the copper. Reflowing the plated deposit by exposing the system to heat, actually initiated the diffusion process during the plating process. There appeared to be no benefit to reflowing the tin top-coat when it came to enhancing either the adhesion of the plated system or the performance of the system in areas such as solderability and contact resistance.

Temperature-Humidity testing was also performed on all the samples per SAE/USCAR-2 using a base temperature of 85°C^[6]. All of the samples passed the contact resistance tests, maintaining a contact resistance value of less than 10 milliohms. All samples were visually inspected and no indication of "white rust" was observed on any of the coupons.

Conclusion

Test results show that, with the correct layered plating system, zinc as well as copper, base material can pass many of the physical tests required by today's electrical component manufactures. Zinc's affinity for fast diffusion of copper and its inherent lack of hardness and spring mechanics make it a less than suitable base metal for certain applications. With that said, there are certain applications where zinc, with the proper electroplated finish, can be a viable low cost alternative to copper and copper alloys. This study touches on a possible coating system but more work needs to be performed in an effort to better define an efficient layered finish. Likewise, more work needs to take place with regards to zinc and zinc alloy material. Research for this paper led to information regarding zinc alloys that may impede the quick diffusion characteristics recorded in this study. Alternative zinc alloys should be considered along with some of the plated layered systems discussed in this paper.

Zinc and zinc alloys should be considered as a viable alternative to copper and copper alloys for use in certain electrical applications. Particular attention should be given to the thermal conditions these systems are exposed to when selecting zinc as a basis metal.

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Sample	Room Temp.				85°C			125°C			150°C		
	As Plated	24 hrs.	168 hrs.	1,008 hrs.	24 hrs.	168 hrs.	1,008 hrs.	24 hrs.	168 hrs.	1,008 hrs.	24 hrs.	168 hrs.	1,008 hrs.
1	P	P	P	P	P	P	P	P	F	F	F	F	F
2	P	P	P	P	P	P	P	P	P	P	P	P	P
3	P	P	P	P	P	P	F	F	F	F	F	F	F
4	P	P	P	P	P	P	F	F	F	F	F	F	F
5	P	P	P	P	P	P	P	P	P	F	P	F	F
6	P	P	P	P	P	P	P	P	P	P	P	P	P

Figure 1

Solderability Results at 85°C

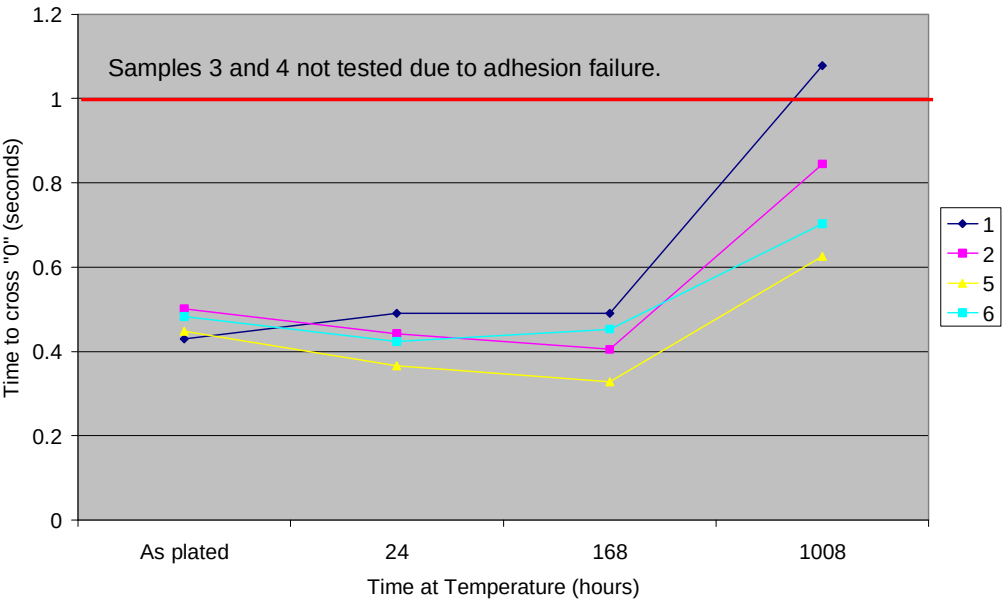


Figure 2

Solderability Results at 125°C

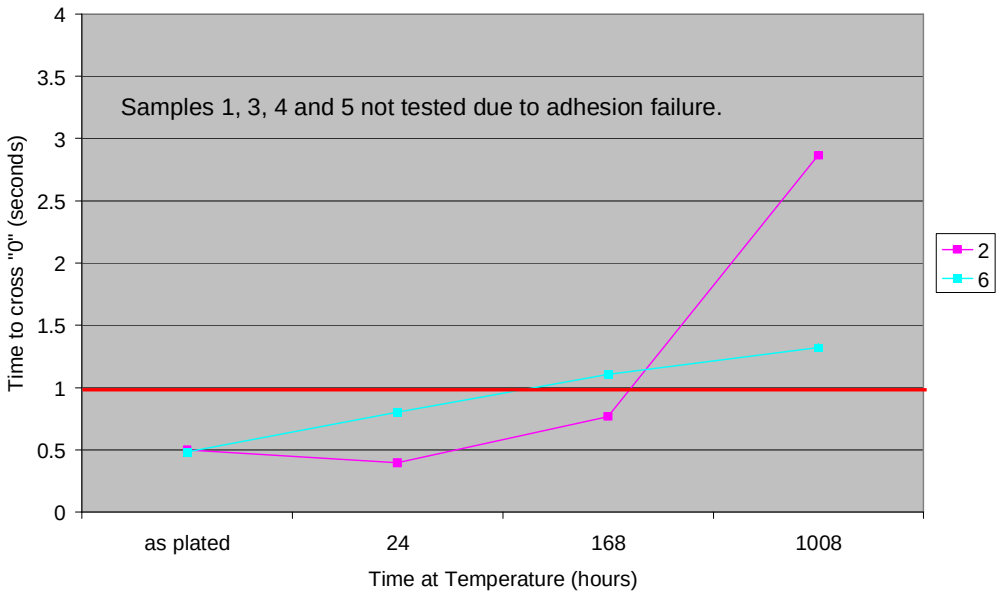


Figure 3

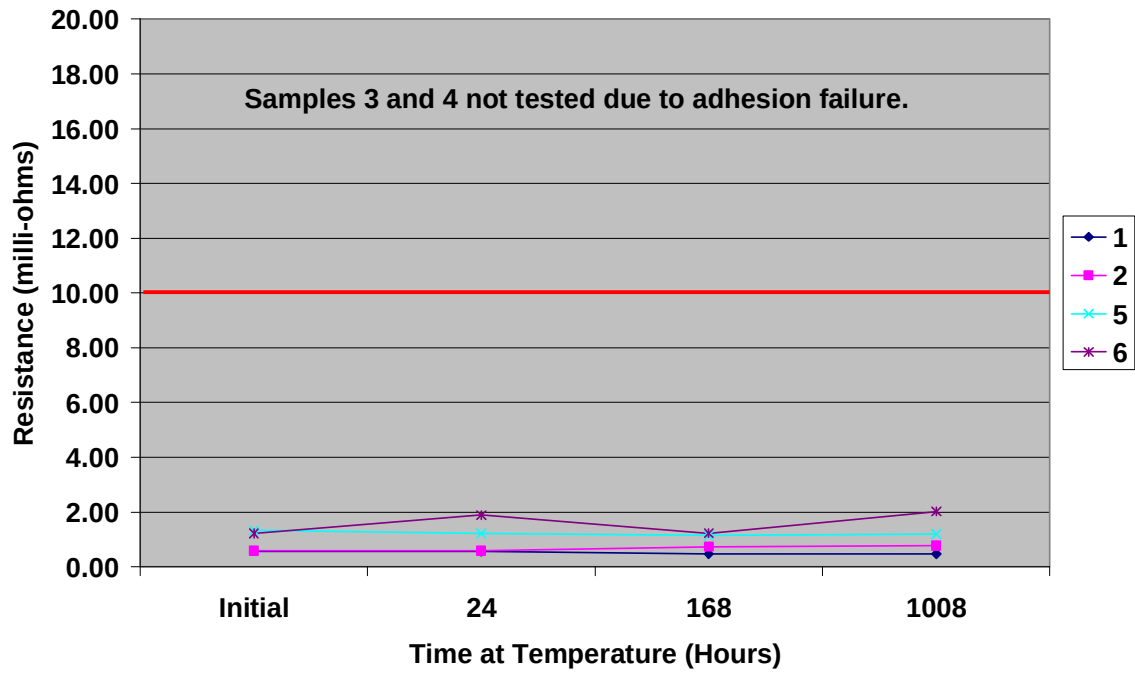
85°C Contact Resistance Testing

Figure 4

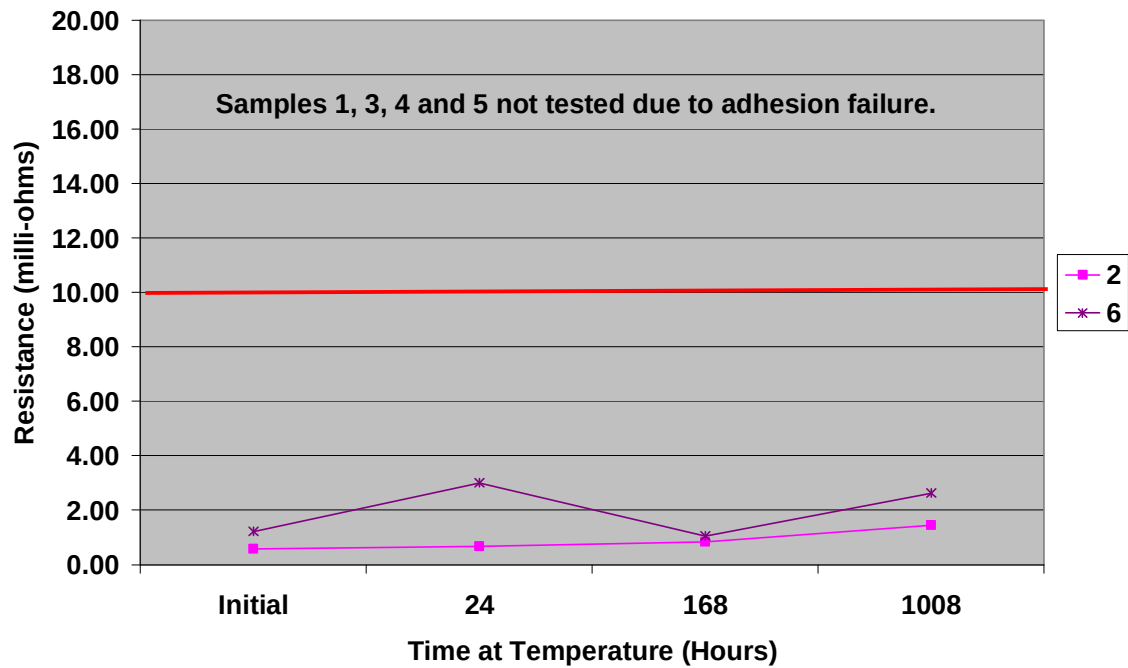
125°C Contact Resistance Testing

Figure 5

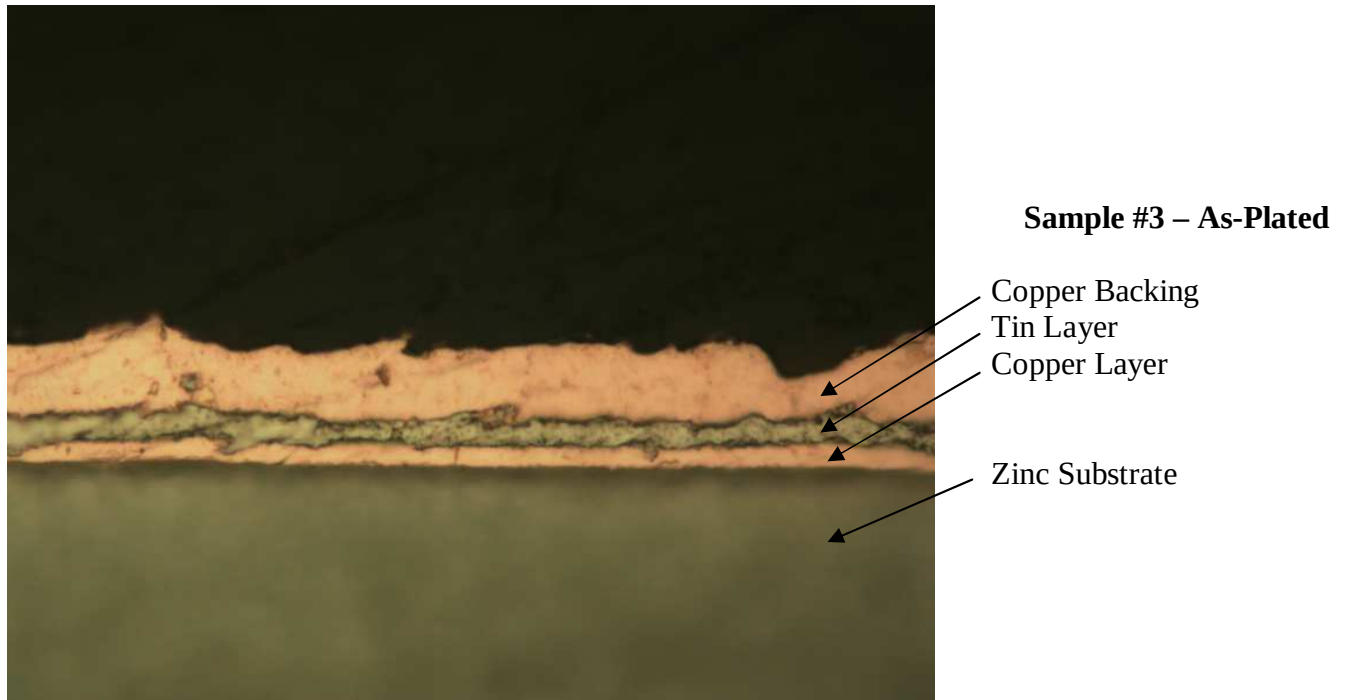


Photo 1

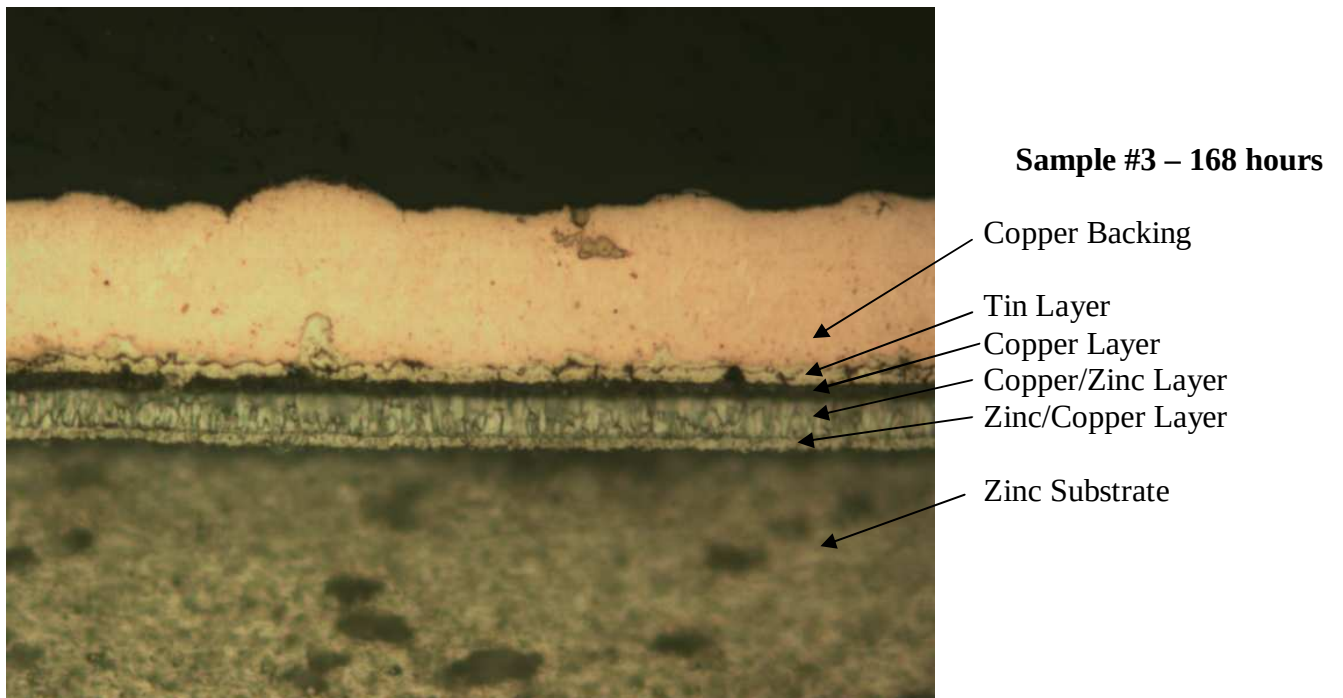


Photo 2

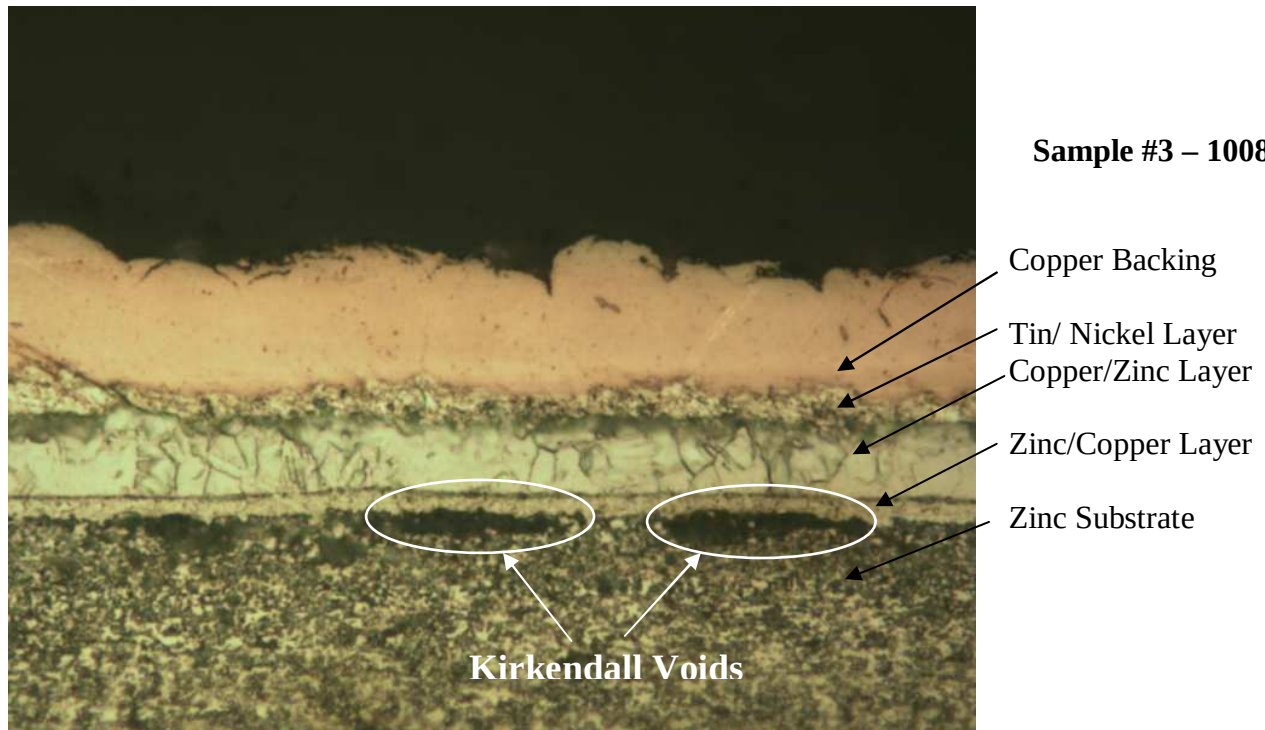


Photo 3

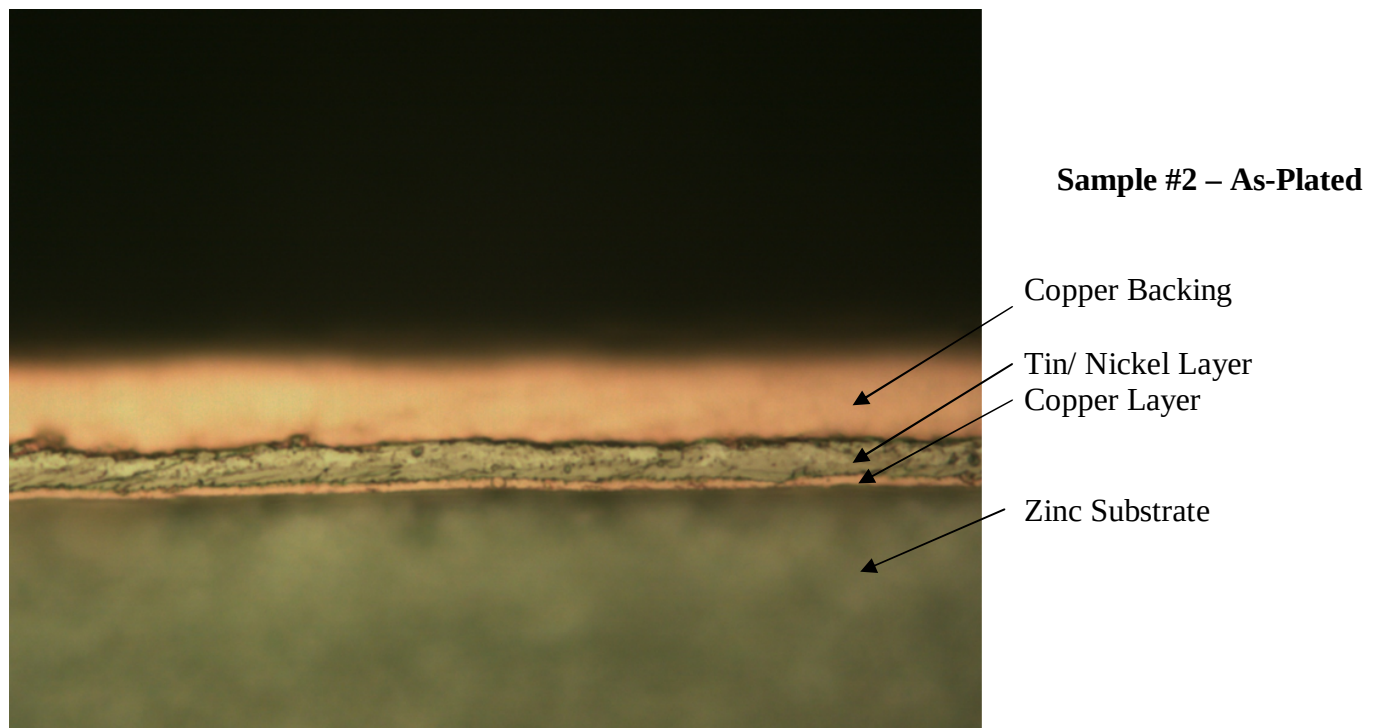
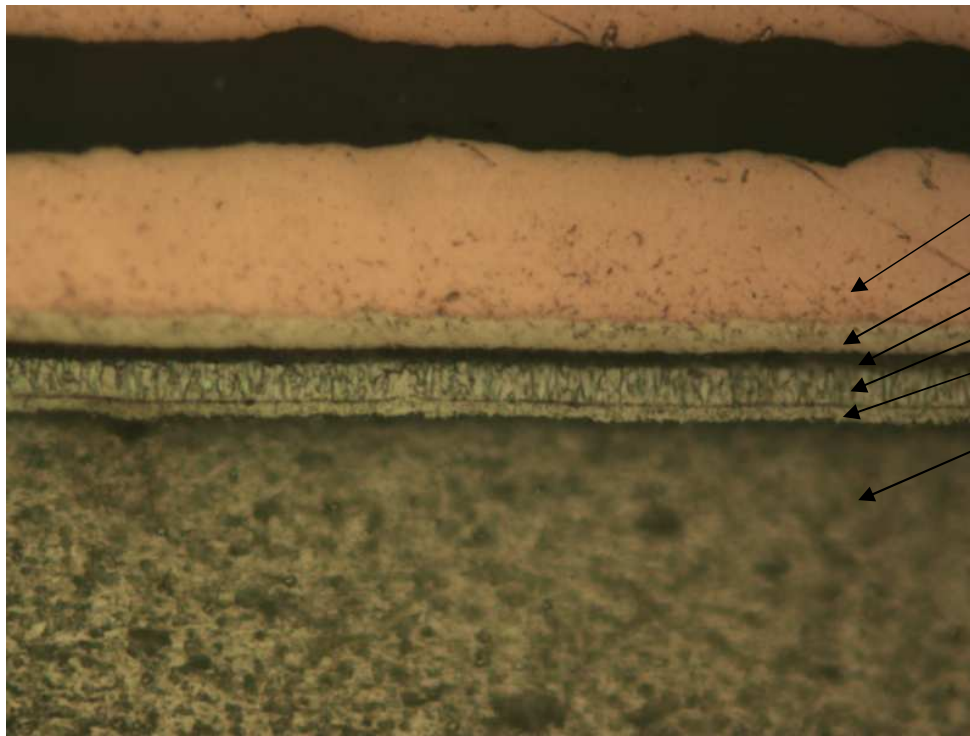


Photo 4



Sample #2 – 168 hours

Copper Backing

Tin/ Nickel Layer

Copper Layer

Copper/Zinc Layer

Zinc/Copper Layer

Zinc Substrate

Photo 5



Sample #2 – 1008 hours

Copper Backing

Tin/ Nickel Layer

Copper/Zinc Layer

Zinc/Copper Layer

Zinc Substrate

Photo 6

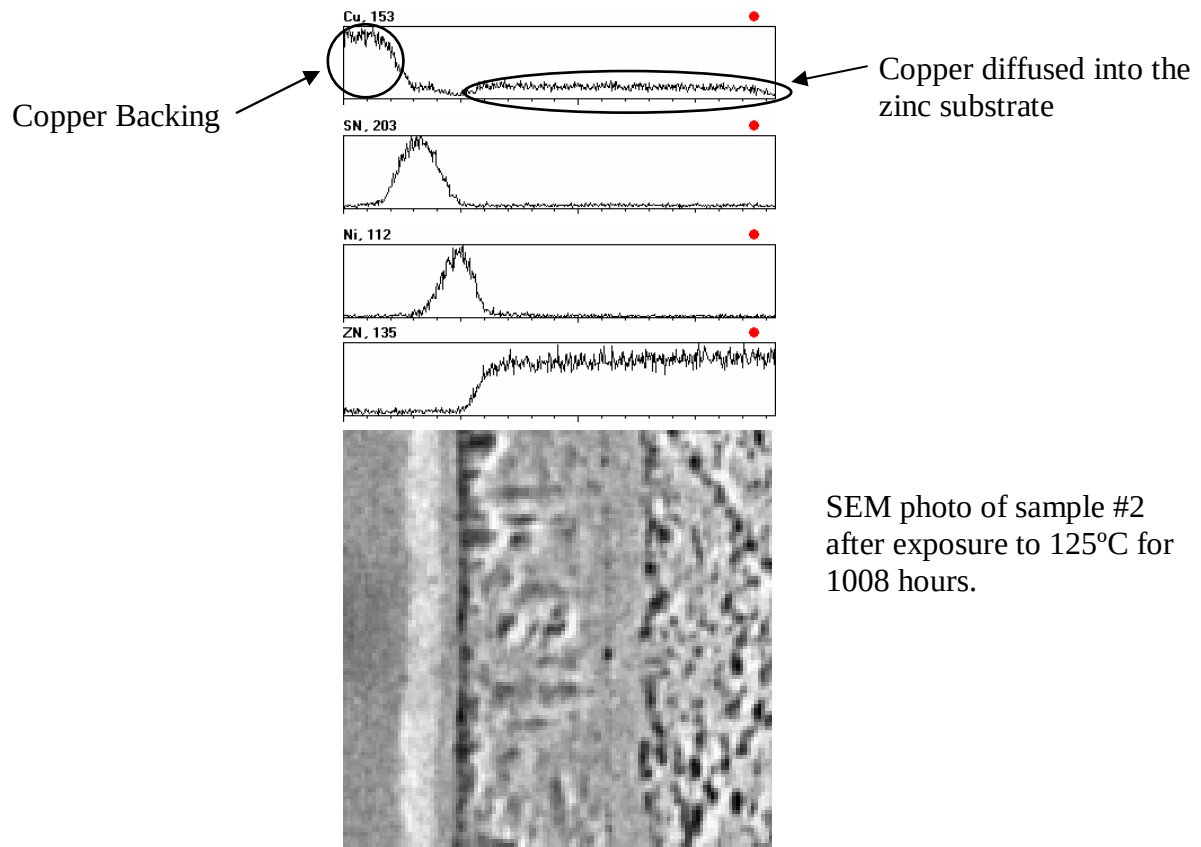


Figure 6

^[1] James Carbone, "Price forecasting is becoming critical to many OEMs because forecasts often have a direct impact on the bottom line.", Purchasing, April 2008.

^[2] ASTM B 539-80 Standard Method For Measuring Contact Resistance Of Electrical Connections (Static Contacts), American Society For Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, 1980

^[3] MIL-STD 883, Method 2003 Standard Practices for Evaluation of Electronic Components...

^[4] E.O. Kirkendall, "Diffusion of Zinc and Alpha Brass", Trans. Metallographic Society AIME, 171, 130 (1947)

^[5] Jack W Dini, "Electrodeposition – The Materials Science of Coatings and Substrates" Noyes Publications, reprint edition, New Jersey, Chapter 4, pg. 94, 1993.

^[6] SAE/USCAR, Performance Specification for Automotive Electrical Connector Systems, 5.6.2 Temperature/Humidity Cycling, Revision 4, ISBN: 0-7680-0114-5, Issued August 1997, Revised May 2004.