High Throw DC Acid Copper Formulation for Vertical Continuous Electroplating Processes

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ABSTRACT

The electronics industry has grown immensely over the last few decades owing to the rapid growth of consumer electronics in the modern world. New formulations are essential to fit the needs of manufacturing printed circuit boards and semiconductors. Copper electrolytes for high throwing power applications with high thermal reliability and high throughput are becoming extremely important for manufacturing high aspect ratio circuit boards.

Here we discuss innovative DC copper metallization formulations for hoist lines and VCP (Vertical Continues Plating) applications with high thermal reliability and throughput for high aspect ratio PCB manufacturing. The formula has a wide range of operation for current density. Most importantly plating at high current density using this DC high throw acid copper process offers high throughput, excellent thermal reliability, and improved properties for present-day PCB manufacturing. The operating CD range is 10 – 30 ASF where microdistribution of ≥ 85 % for AR 8:1 is achievable. This formulation offers bright ductile deposits where plating parameters are optimized for improved micro-distribution and the properties of the plated Cu deposit such as tensile strength and elongation. The thermal reliability and properties of the deposits were examined at different bath ages. Measured properties are Elongation ≥ 18% and tensile strength ≥ 40,000 psi. All the additives can be easily controlled by Cyclic Voltammetry Stripping analysis

Key words: Copper electroplating, PTH, PCB metallization.

Introduction

Copper has ~~a~~ high electrical conductivity and is relatively inexpensive compared to other high conductive metals such as Silver. Therefore, the use of copper in the mass production of printed circuit boards (PCB) and semiconductors grew exponentially in the last few decades[1].With today's complex circuit board designs an even deposition with specific physical properties is necessary to meet the standards. Especially with high aspect ratios, through hole plating to obtain desired plating distribution is much more challenging. During the quality control inspection, a board can be rejected if there is insufficient copper on the center walls of the through holes. Moreover, plated copper should meet the minimum requirements of physical properties such as tensile strength and elongation (T&E), to withstand the high temperature applications. [2]

Sulfuric acid copper baths are heavily used in the PCB industry due to their low maintenance cost as compared to other acids like MSA (methane sulfonic acid).Typical sulfuric acid copper baths contain copper sulfate, sulfuric acid, chloride ions, and organic additives. These additives play a crucial role in controlling the deposit distribution as well as the properties. To meet specific objectives of a plating process these additives should be monitored and controlled properly. The additives work in combination and when controlled within a given range improve thickness distribution, mass transfer, eliminate nodule formation and also can fill blind vias. Namely these additives are Levelers, Brighteners, and Suppressors. The leveler is a mild suppressor that adsorbs onto specific locations such as corners and peaks of base materials [2].

In the presence of a micro profile the diffusion layer tends to be thin at the peaks and thick at the valleys. In this case if plated without a leveler the micro profile will be exaggerated. On the other hand, if a leveler is present the plating on the peaks will be suppressed and the micro profile will be diminished. Brightener is also called an anti-suppressor and as the name implies it reduces the suppression. Most importantly it also acts as a grain refiner to deposit copper with a fine grain structure in random orientation [4] Therefore, brightener has the most influence on final structure and physical properties of the deposit such as tensile strength and elongation.

The suppressor works in the presence of chloride ion to adsorb on to the cathode and increase the effective thickness of the diffusion layer [3]. As a consequence, the plating current increases and the deposit becomes more uniform and a densely packed copper deposit can be obtained without burning. This modified diffusion layer improves the distribution of the deposit especially in high throw applications. Owing to the growth of high aspect ratio circuit board manufacture, the demand for high throw acid copper electrolytes has increased dramatically over the past few decades. Especially DC copper plating for high aspect ratio electroplating is extremely desirable due to simplicity of the process and inexpensive equipment requirements. [1, 2]

In this work, we present an innovative DC high throw acid copper electroplating system with high thermal reliability and even copper metallization in high aspect ratio PCBs. This system also allows the plating to be done at high current density without surface imperfections. The allowable CD for ranges from 10 – 30 ASF with the Micro Distribution (MD) measured is≥ 85% for the AR 8:1.

Numerous tests were performed to obtain high Micro Distribution at various current densities with enhanced mechanical properties of the plated metal such as tensile strength and elongation. Thermal reliability and structure of plated Cu was also studied.

CONDITIONS AND BATH COMPONENTS

Table 1 shows the operational conditions and optimum additive levels. Typically the high throw bath has high acid to achieve higher conductivity inside the holes.

TABLE 1. Bath components

Parameter	Range	Optimum
Anode Current Density	1.0 – 3.5 ASD (10-32 ASF)	2.2 ASD (20 ASF)
Temperature	20 - 27ºC (68 - 80ºF)	23ºC (73ºF)
Material A Wetter	3 - 8 mL/L	5 mL/L
Material A Brightener	0.7 - 1.3 mL/L	1 mL/L
Material A Leveler	7 – 13 mL/L	10 mL/L
Copper Sulfate ($CuSO_4$.**5** (_ H_2O)	60 - 80 g/L	70 g/L
Free Sulfuric Acid 66^{o}Be Electronic Grade	190 - 210 g/L	200 g/L
Chloride Ion (Cl^-)	50 – 70 ppm	60 ppm

TEST VEHICLES

Various test panels with different thickness and hole diameter were used covering a range of aspect ratios. The test vehicles used in the process evaluation were 1.6 mm, 2.4 mm, and 3.2 mm thick boards and the through hole diameters were 0.2 mm, 0.25 mm, and 0.35 mm. The through hole Aspect Ratio (AR) varied from 4.6 to 16. All geometries for each test board thickness were plated at the same time in the same tank and later throw power was calculated by using cross section analysis.

The process flow included the following operations:

- Acid cleaner: Wets the hole and remove any organic contaminants.
- DI water rinse
- Micro-etch: Further smooths the surface and ensures excellent copper to copper adhesion.
- DI water rinse
- Acid dip: Acidifies copper surface prior to plating.
- Electroplating of copper in acid copper bath

CROSS SECTION ANALYSIS

Cross section analysis was started with the sample preparation process by punching or routing sections from a desired area on the board or test panel. Pre-grinding of the coupon was done to get a flat surface closer to the through holes. Plastic index pins were used to align the coupon vertically to the grinding surface. A fast-cure acrylic resin was used to mount the coupons. A ratio of 1-to-1, hardener-to-resin, was used to provide optimum penetration and a quick cure rate (10-15 minutes). After the section hardened they were subjected to grinding, polishing, and microscopic inspection to obtain Micro Distribution. Figure

1 shows a cross section of a through hole indicating the points of thickness measurements.

MICRODISTRIBUTION

The Micro Distribution is defined as the ratio of the average copper deposit thickness in the center of the through hole to the average copper deposit thickness at the surface. It is calculated according to the following equation:

$$Microdistribution = \frac{(C + D)/2}{(A + B + E + F)/4} \, x \, 100\% \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad \boldsymbol{Eq\ 1}$$

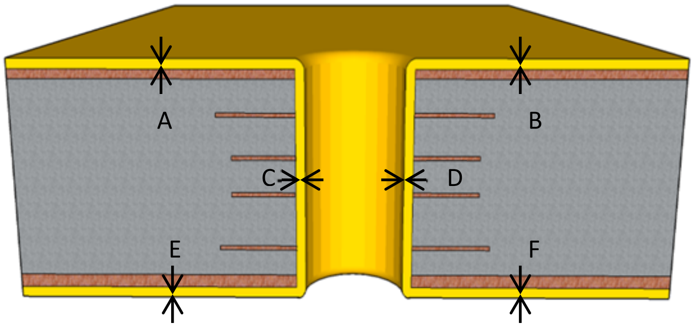

Figure 1. Cross Section of Plated Panel

RESULTS

MICRODISTRIBUTION

Micro Distribution (MD) is the ratio between the average plated thicknesses in the middle of the hole to the average plated thickness on the surface as shown in Figure 1. Care should be taken when using MD % due to the difference in the board thickness, as the same diameter hole will be more difficult to plate in the thicker board as shown in Figures 2, 3, and 4. At the same current density, the same diameter hole has lower MD in a thicker board. For instance, 0.2 mm hole in a 1.6 mm board at 10 ASF gave 90 % Micro-Distribution measurement, while 0.2 mm hole in a 2.4 mm board at 10 ASF gave only 75 % MD measurement. Furthermore 0.2 mm hole in a 3.2 mm board gave 61 % MD . Therefore aspect ratio should be used to define the difficulty of the plating.

Another crucial factor which determines the Micro Distribution % is the mass transfer, which is directly proportional to the diffusion. While several factors influence diffusion one significant factor is current density at which the plating is done. At high cathodic current density, the abundance of electrons at the cathode accelerates the reduction reaction of cu ions to cu metal at the cathode. Due to this the Cu ions in the diffusion layer will exhaust rapidly. If the cu ions in the diffusion layer continue to drop without a replenishment from the bulk electrolyte the deposit could show severe surface burning and cause poor distribution. On the other hand at relatively low current density the plating rate will be low with the depletion of cu ions in the diffusion layer due to the reduction reaction. Since the plating rate is low there will be enough time for the cu ions in the bulk electrolyte to replenish the diffusion layer. Owing to this equilibrium there will be an even distribution and no burning will occur.

This phenomenon is clearly shown in Figures 2, 3, and 4. As an example in Figure 2, at 10 ASF 0.35 mm hole showed 99% Micro Distribution whereas when the CD increased to 20 ASF the MD dropped to 95 % for the same hole in the same board thickness and further at 30 ASF the MD dropped to 87 %.

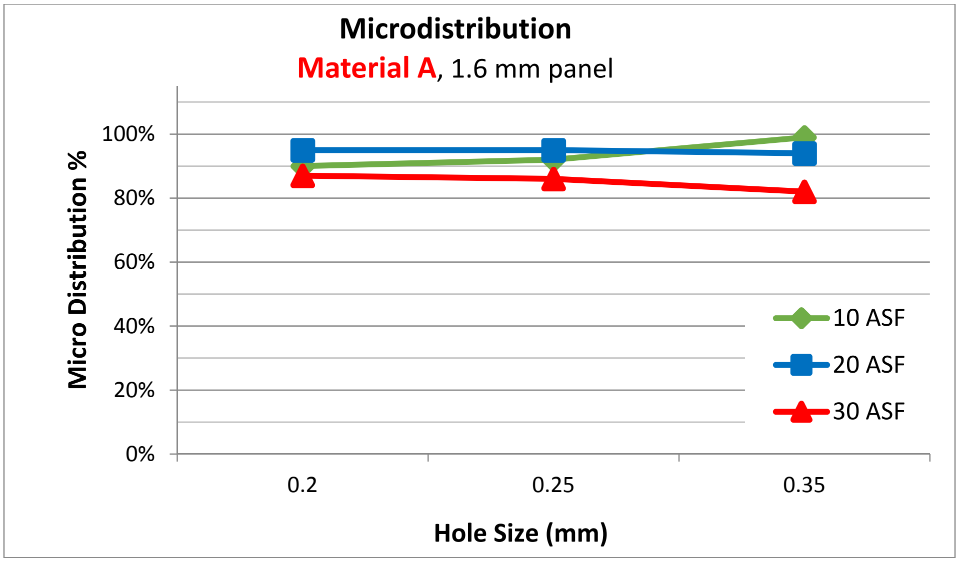

Figure 2. Microdistribution for 1.6 mm Thick Panel Aspect Ratio: 8, 6.4, and 4.6

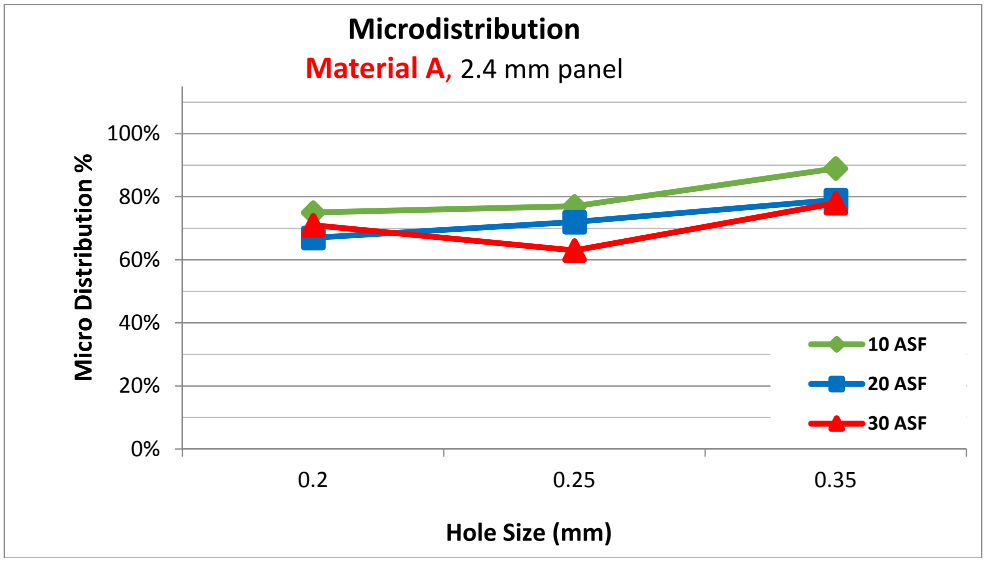

Figure 3. Microdistribution for 2.4 mm Thick Panel Aspect Ratio: 12, 9.6, and 6.9

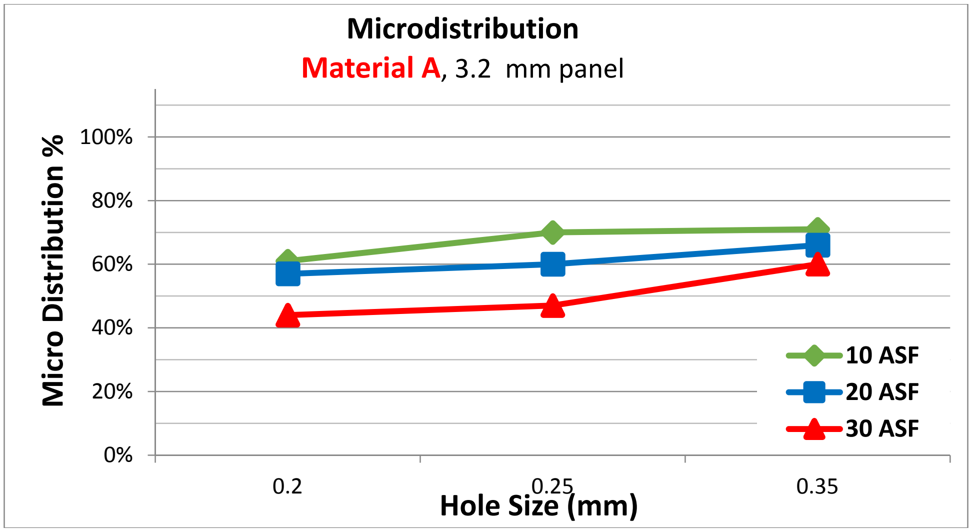

Figure 4. Micro distribution for 3.2 mm Thick Panel Aspect Ratio: 16, 12.8, and 9.1

SURFACE, STRUCTURE, AND MORPHOLOGY

All the plating conditions produced smooth, ductile, uniform, and mirror bright surfaces. Excellent leveling was seen inside the hole as shown in Figure 5. Further Figure 5 shows show no thin copper at the knee in the cross sectional images for the 1.6 mm thick board plated at current densities 10, 20, and 30 ASF respectively. Uniform fine grained copper layers throughout the hole is observed. After the microscopic evaluation the sections were further evaluated using scanning electron microscopy (SEM). Figure 6 shows the results from the SEM analysis where three different areas were analyzed; inside the hole, corner, and the surface. Despite the current density difference at the corner and inside the hole or at the surface, the morphology shows the same fine equiaxial grains. No preferred orientation like columnar grains were observed.

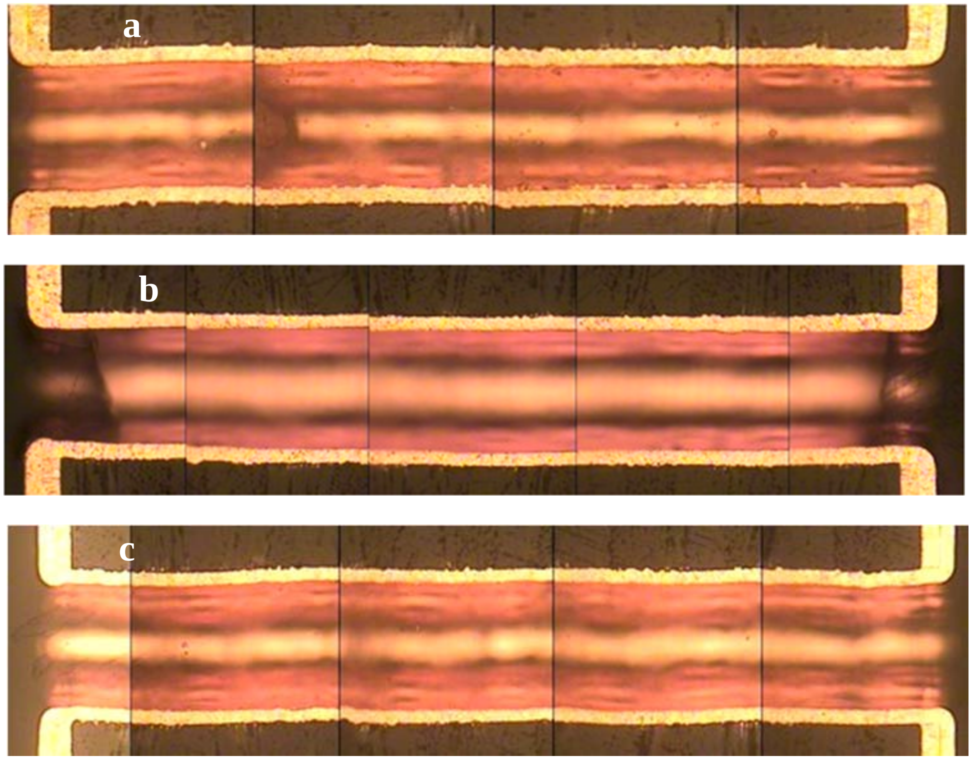

Figure 5. Cross Sections of Through Holes plated at a) 10 ASF ; b) 20 ASF; c) 30 ASF; 1.6 mm Test Panel

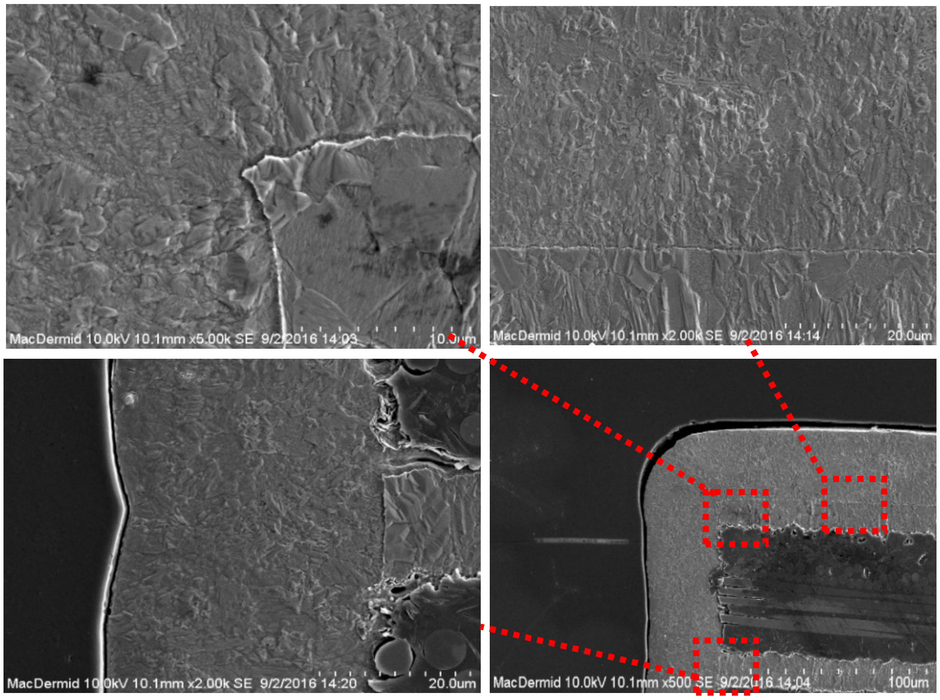

Figure 6. Scanning electron microscopy (SEM) of IST 22 Layer Through Holes plated at 10 ASF with 2.4 mm Test Panel

PHYSICAL AND THERMAL PROPERTIES

Final deposit plated under the influence of additives suppressor, grain refiner, and leveler will show characteristic physical properties. These properties also depend on the plating rate or current density, temperature at which the plating is done and the morphology. For instance, densely packed equiaxial deposit will have better physical properties than columnar deposit. Most important to PCB manufacturing are tensile strength and elongation%, where these properties show the tolerance of the deposit for thermal stress.

$$Mean\ average\ cross\ sectional\ area\ (in2) = \frac{Weight\ of\ the\ sample\ (lbs)}{Length\ of\ tensile\ sample\ (in)x\ density\ of\ copper\ (g/in3)} \ldots \boldsymbol{Eq\ 2}$$

$$Tensile\ Strength\ = \frac{Maximum\ load\ (lbs)}{Mean\ cross\ sectional\ area\ (in2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \boldsymbol{Eq\ 3}$$

$$Elongation\ = \frac{(Length\ at\ break - Original\ gage\ length)}{Original\ gage\ length}\ x\ 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \boldsymbol{Eq\ 4}$$

Physical properties were measured according to the IPC TM-650, 2.4.18.1 test method. Sample strips were extracted and baked in an oven at 125 °C for four to six hours. An industry mechanical test instrument was used to test the strips. The measurements were used to calculate tensile strength and elongation % using equations 2, 3, and 4. Table 2 shows the results at two different bath ages, fresh bath and bath aged around 50 Ah/L. According to the results properties did no change much with the bath age.

TABLE 2. Physical properties

Property	Fresh Bath	Aged Bath
Tensile Strength (psi)	43,120	44,470
Elongation %	22.18	26.35

Further, to evaluate thermal characteristics of the deposit the 6X solder shock resistance test was performed on plated through holes in accordance with IPC TM-650 2.6.8. Solder shock(SS) conditions were 10 seconds float at 288ºC for 6 times on the same side of the test coupon. Results are shown in Figure 7/ After 6X SS testing, no corner cracks, barrel cracks, or hole wall pull away was observed.

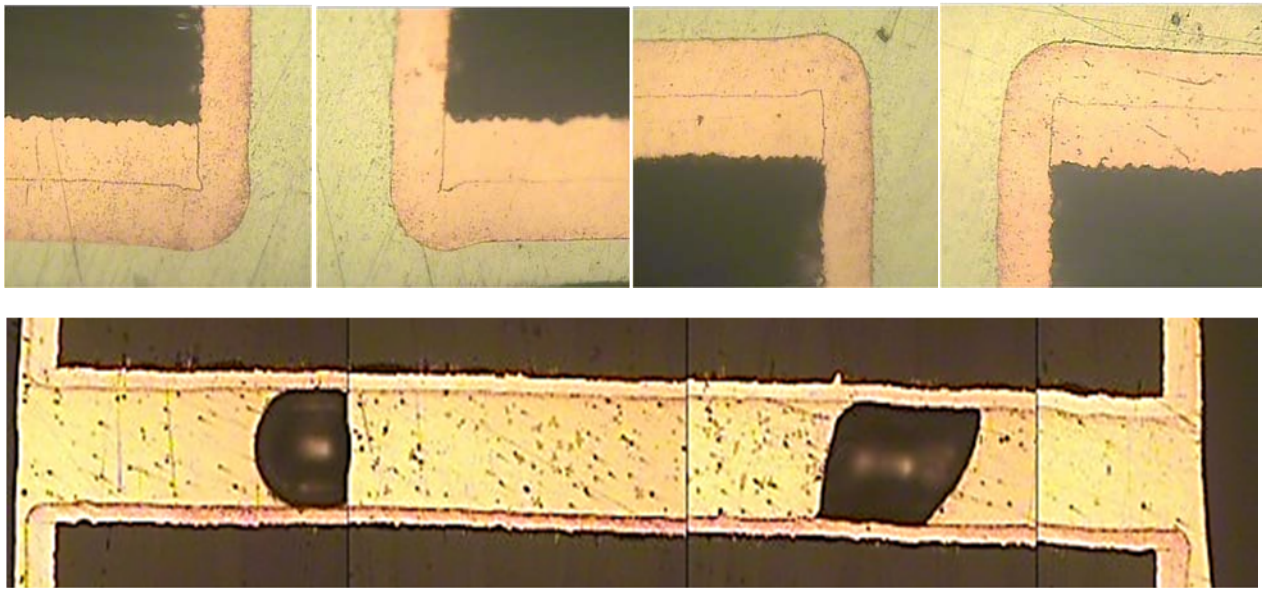

Figure 7. 6X thermal shock test

Interconnect Stress Testing (IST) was also carried out to further characterize the deposit. IST testing is an accelerated test method used to evaluate the integrity of interconnects and plated through holes. This method utilizes electrical currents passed through a circuit in the board at sufficient resistance to increase temperature. Coupons were run through assembly simulation called preconditioning prior to cycling. Coupons were tested prior to preconditioning for continuity. Figure 8 shows the assembly of through holes in an IST coupon and the electrical continuity.

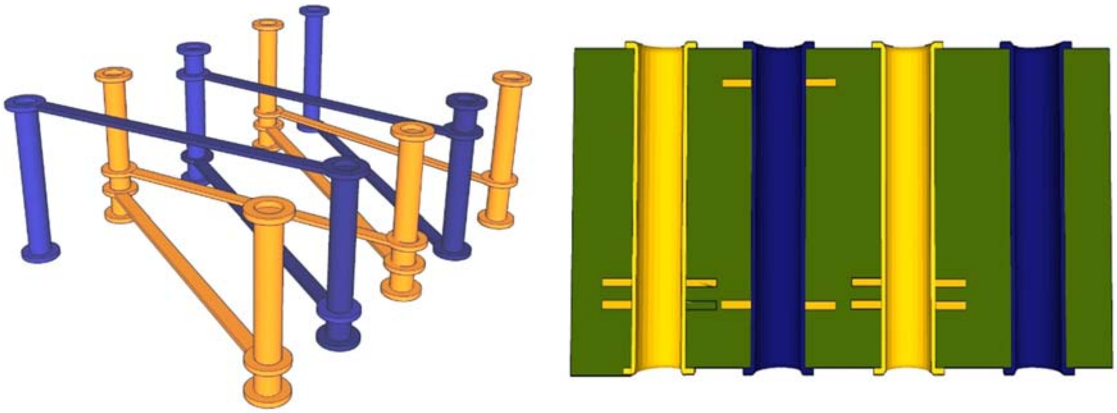

Figure 8. Assembly of through holes in an IST coupon. Power is shown in gold and the sense is in blue.

A coupon was sacrificed to determine the current needed for pre-conditioning. All coupons were preconditioned six times to 260 °C prior to cycling at 150 ºC to 500 cycles or to failure. After preconditioning, baseline resistance readings were established and the temperature cycling was started. Each thermal cycle consists of passing sufficient current through the internal power circuit to elevate the temperature to 150ºC, then subsequent cooling down to ambient temperature. During the temperature cycling, resistance is monitored on the power circuit and the sense circuit. If the resistance is >10% over the established baseline on either circuit, it is considered a failure and the test is halted. Material type and complexity of the build have an influence on the cycles to failure. Table 3 shows the results from the IST test and all 5 coupons tested passed the 500 cycles test. This test also confirms and agreed with the 6X solder shock test. Figure 9 shows a cross section of a through hole with 22 layers extracted from the IST test panel after plating

TABLE 3. Interconnect Stress Testing (IST) data

<table>
<tr><th colspan="6">Material A bh, p2-s2, 6xpre cond_dat.csv</th></tr>
<tr><td>Coupon #</td><td>#2</td><td>#4</td><td>#6</td><td>#9</td><td>#11</td></tr>
<tr><td>Cycles</td><td>500</td><td>500</td><td>500</td><td>500</td><td>500</td></tr>
<tr><td>%P</td><td>0.430</td><td>0.267</td><td>0.405</td><td>0.264</td><td>0.462</td></tr>
<tr><td>%S</td><td>1.243</td><td>1.240</td><td>3.038</td><td>2.878</td><td>1.392</td></tr>
<tr><th colspan="6">Material A - p2s2, 6xpre_dat.csv</th></tr>
<tr><td>Coupon #</td><td>#2</td><td>#3</td><td>#6</td><td>#9</td><td>#11</td></tr>
<tr><td>Cycles</td><td>500</td><td>500</td><td>500</td><td>500</td><td>500</td></tr>
<tr><td>%P</td><td>0.000</td><td>-0.380</td><td>0.072</td><td>-0.462</td><td>-0.393</td></tr>
<tr><td>%S</td><td>-0.070</td><td>-0.280</td><td>-0.069</td><td>-0.355</td><td>-0.591</td></tr>
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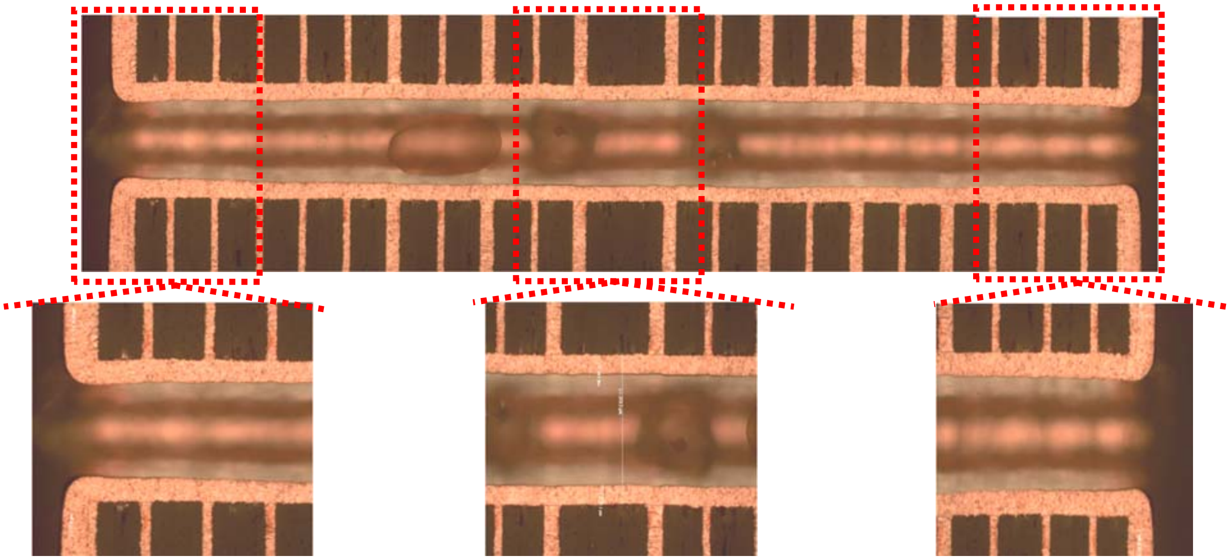

Figure 9. Cross Sections of IST 22 Layer Through Holes plated at 10 ASF with 2.4 mm Test Panel

CONCLUSIONS

An excellent formula was developed for DC copper metallization for hoist lines and VCP (Vertical Continues Plating) applications. The operating CD range is 10 – 30 ASF where, Micro Distribution of ≥ 85 % for AR 8:1 is achievable. Deposits were bright and ductile and also met IPC standards for the properties such as tensile strength and elongation. The thermal characteristics of plated copper also met the IPC standards and showed no failure during the solder shock tests. Coupons also passed the 500 cycles in IST testing. All the organic additives can be easily monitored by industry **Cyclic Voltametry Striping Analysis**

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