NASA DoD Phase 2
Report for SAC305 & SN100C Copper Dissolution Testing

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Table of Contents

Introduction

Copper dissolution is a concern for products making the conversion to lead-free solder alloys. In these alloys, the reaction of the tin/copper is much faster than that of tin-lead solders/copper, which increases the degradation of the plated copper connections. Since no copper dissolution testing was conducted during Phase 1 of the JCAA/JGPP program testing, which focused on the reliability of solder joints, Phase 2 included testing to validate copper dissolution measurements report by the commercial electronics industry. Copper dissolution is of particular concern if components are to be reworked, which is much more commonly used on high-reliability electronics than in consumer electronics. Reworking product that has lead-free solder joints may impact the repair depot operations as the copper dissolution may remove over half of the Plated Through Hole (PTH) copper in a single rework cycle. Multiple rework cycles may not be acceptable for lead-free products due to copper dissolution impact.

Test Vehicle

The test vehicle used for the copper dissolution testing was a modified Interconnect Stress Test (IST) PTH reliability coupon. Four plated through hole, dual in-line package (PTH DIP) patterns and two surface mount technology quad flat pack (SMT QFP) patterns were added to the IST coupon design for the copper dissolution testing. Figure 1illustrates the copper dissolution test coupon used in the testing efforts.

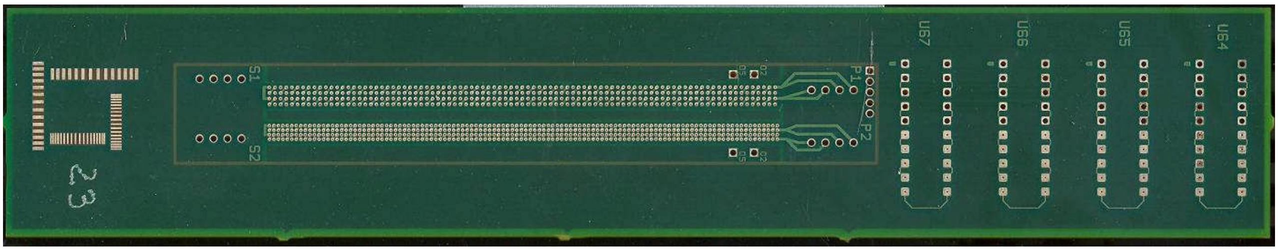


Figure 1: NASA DoD Copper Dissolution Test Coupon

The test coupon, which was approximately 2” x 9” and 0.092” thick, was fabricated with an IPC-4101/26 laminate (Isola 370 HR) with a 170°C Tg minimum material. The coupon surface finish was immersion silver (MacDermid Sterling 0.2-0.4 microns). Two PTH sizes were used: 0.036” and 0.015” finished diameter.

Test Machine & Solder Alloy

An Air-Vac PCBRM12 Solder Fountain mini-pot wave machine was used for this test. A FWL-1248 nozzle was used for the SMT QFP footprint and a FWL-2448 nozzle was used for PTH DIP footprint. Both nozzles were a rectangular fountain type nozzle that completely covered the SMT QFP footprint and covered three PDIP component footprints. Two solder alloys were used: SAC305 (supplied by AIM [1]) and SN100C (Nihon Superior) with one at each of the two test facilities included in this study. Table 1 lists the solder alloy test information.

Solder Alloy	Wave Pot Temperature	Test Facility
SAC305	260°C	Celestica
SN100C	270°C	Rockwell Collins

Table 1: Solder Alloy Test Information

The wave height and contact area were validated using a quartz glass plate. Thermocouples were used to record temperature profiles for each of the timed exposures, which were conducted in an air environment. Figure 2 illustrate the wave solder setup.

Figure 2: Wave Solder Equipment Setup

Experimental setup

A fixture was fabricated to support the test vehicle for the exposures. This provided a stable platform for repeating the cycles and minimizing any setup variability. Each exposure was thermal profiled using embedded thermocouples located at the PTH base, mid-point, and top locations. The machine/fixture and the thermocouple setup are shown in Figure 3. The solder flow rates were held constant across the various exposures.

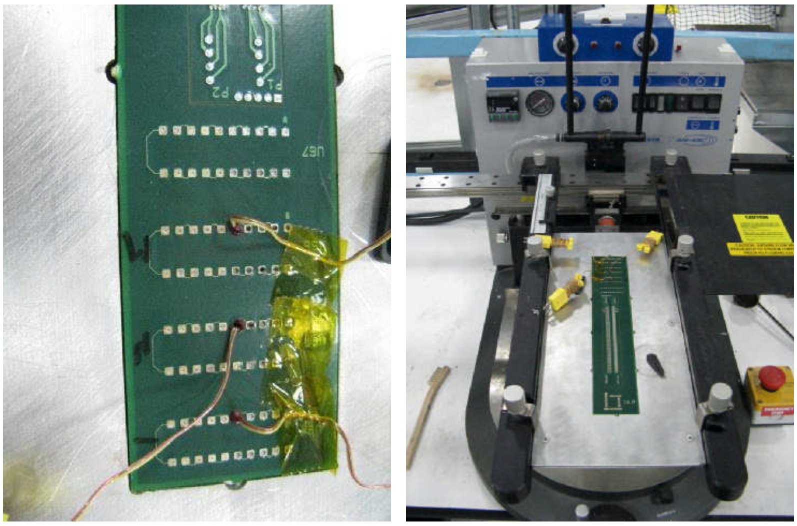


Figure 3: Left - Thermocouple Placement; Right - Wave Solder Equipment with Test Coupon

A total of 32 test vehicles per alloy were subjected to various exposure times and number of cycles. In the SAC305 testing, one location of the test vehicle (PTH DIP U67) was taped off with Kapton tape to preserve the copper baseline data for that serial number card. In the SN100C testing, the baseline copper thickness was determined by measuring the thickness of copper under those samples that had Electroless Nickel Immersion Gold (ENIG) surface finish. The test matrix is listed in Table 2.

Coupon ID	PTH Contact Time	# PTH cycles	Total PTH Exposure	SMT Contact time all in one cycle
190	80	3	240	120
191	80	3	240	120
170	35	2	70	40
171	35	2	70	40
172	35	2	70	40
173	35	2	70	40
174	35	2	70	40
175	35	3	105	50
176	35	3	105	50
177	35	3	105	50
178	35	3	105	50
179	35	3	105	50
180	40	2	80	15
181	40	2	80	15
182	40	2	80	15
183	40	2	80	15
184	40	2	80	15
185	40	3	120	20
186	40	3	120	20
187	40	3	120	20
188	40	3	120	20
189	40	3	120	20
165	40	1	40	10
166	40	1	40	10
167	40	1	40	10
168	40	1	40	10
169	40	1	40	10
41	40	4	160	25
42	40	4	160	25
43	40	4	160	25
44	40	4	160	25
45	40	4	160	25

Coupon ID	**Through Hole Wave Exposure (s)**	**Surface Mount Wave Exposure (s)**
35	240+Baseline (14)	120
39	240+Baseline (14)	120
50	160+Baseline(14)	50
51	160+Baseline(14)	50
52	160+Baseline(14)	50
53	160+Baseline(14)	50
54	160+Baseline(14)	50
69	120+Baseline(14)	40
70	120+Baseline(14)	40
71	120+Baseline(14)	40
72	120+Baseline(14)	40
73	120+Baseline(14)	40
98	105+Baseline(14)	25
99	105+Baseline(14)	25
100	105+Baseline(14)	25
101	105+Baseline(14)	25
102	105+Baseline(14)	25
103	80+Baseline(14)	20
104	80+Baseline(14)	20
105	80+Baseline(14)	20
106	80+Baseline(14)	20
107	80+Baseline(14)	20
110	70+Baseline(14)	15
111	70+Baseline(14)	15
112	70+Baseline(14)	15
113	70+Baseline(14)	15
114	70+Baseline(14)	15
115	40+Baseline(14)	10
116	40+Baseline(14)	10
117	40+Baseline(14)	10
118	40+Baseline(14)	10
119	40+Baseline(14)	10

Table 2: Test Coupon Exposure Parameters; Left – Celestica, Right – Rockwell Collins

The exposure times selected in developing the test matrix were selected based on the goal of testing 3 rework cycles with a typical cycle of 40 seconds. A test point at 160 seconds was included to include a possible 4th rework cycle. There are many variables that can affect the outcome of the rework process. A number of the most significant of these, including pot temperature, contact time, alloy type, were investigated in this evaluation. Other process variables, such as the mini-pot flow rate, nozzle type, preheat temperature, product internal copper thermal load, component type, and operator technique are potential sources for variance in the rework process that should be included in a complete evaluation of the rework processes.

Copper Dissolution Measurements

The Celestica test coupon copper dissolution data (for SAC305) were measured using cross-sectioning per the following details:

- Measurements were taken at 3 locations on the test coupons.
- The "A" measurements were taken on the SMT QFP pattern.
- The "B" measurements were taken in the 10 hole PTH DIP pattern of those holes that were not exposed (Masked with Kapton Tape) to the mini-pot wave solder (U67=baseline copper measurement time zero).
- The "C" measurements were taken at the 10 hole pattern of the PTH DIP for each of the 10 holes and the averages and variation recorded by group 1-5 and 6-10 in addition to the individual measurements.

The Rockwell Collins test coupon copper dissolution data (for SN100C) were likewise measured using cross-sectioning per the following details:

- PTH DIP measurements were taken at 10 locations for each plated through hole: the top plated through hole knee, ¼ of PTH thickness, ½ of PTH thickness, ¾ of PTH thickness, bottom plated through hole knee. Ten plated through holes were measured on each test coupon. These measurements are the same as those for the Celestica/SAC305 data with the addition of a measurement at the top plated through hole knee.
- SMT QFP measurements were taken at 6 locations for each test footprint: 3 pads exposed to the wave soldering process and 3 pads not exposed to the wave soldering process as a control. All measurements were taken at the center of the pad.

Figure 4 illustrates PTH DIP and SMT QFP cross-sections with the copper dissolution measurement locations and values.

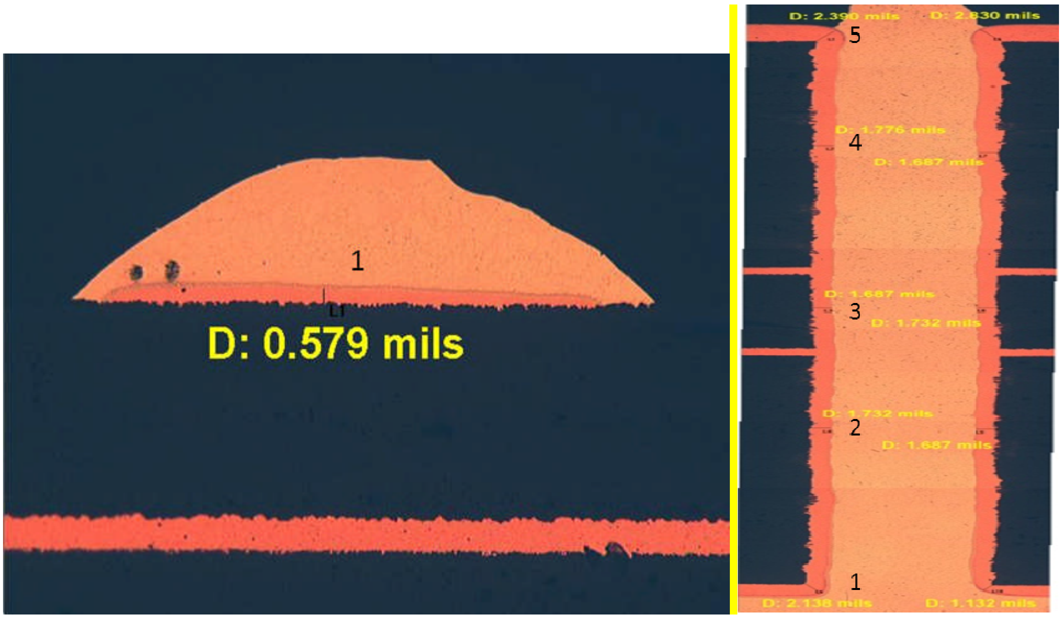
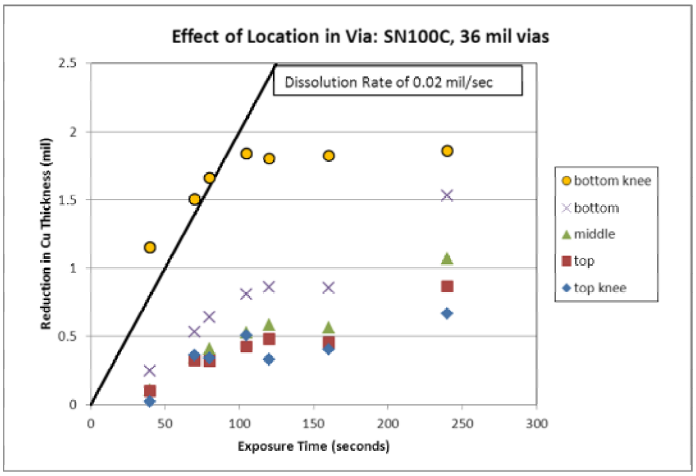


Figure 4: Rockwell Collins Dissolution Measurement Locations; Left - SMT QFP, Right - PTH DIP with Measurement Location Designators Shown

Results

The SN100C solder alloy copper dissolution test results are plotted in Figure 5. The PTH DIP test coupons with the 0.036" holes exhibit a linear dissolution of copper as the wave solder exposure time increases. The PTH DIP test coupons with the 0.015" holes exhibit minimal-to-no copper dissolution even with longer wave solder exposure times. This is considered to be due to the reduced wetting and capillary action in the smaller hole, which was insufficient to allow consistent flow of molten solder up and down the barrel with these alloys. This is not a surprise as the volume of alloy exposure to the copper interface is much greater for the larger hole. Other industry reports show similar results for larger PTH holes. This issue is exacerbated by Design for Manufacturing (DFM) rules for lead-free alloys, which require a larger hole to permit proper hole fill for PTH solder joints[11]. The plated through hole knees for both hole sizes exhibited completed copper dissolution for wave solder exposure times that exceeded ~70 seconds.



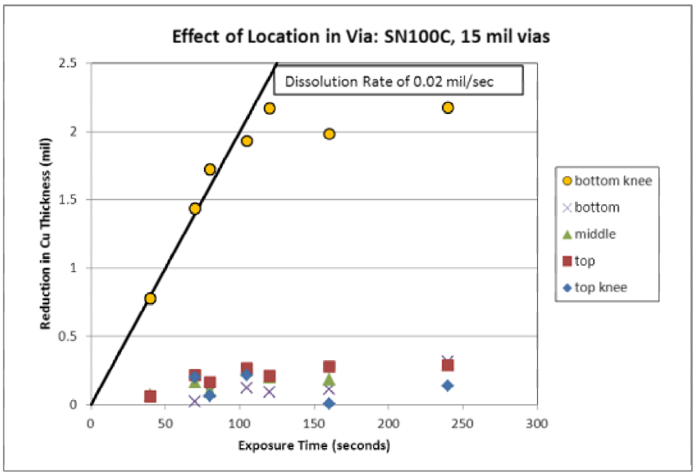


Figure 5: SN100C Copper Dissolution Results; Left - 0.036" PTH, Right - 0.015" PTH

Figure 6 shows a trace that is disconnected from the PTH barrel and therefore represents a board defect resulting from excessive copper dissolution. DFx rules could redirect the location of these signal connections within the barrel towards the upper layers to minimize the risk of an interconnection failure in the product. Figure 7 illustrates a 0.036" PTH that was subjected to a total of 240 seconds of wave solder exposure. The PTH copper has been completed dissolved in the wave soldering process to nearly 30% of the plated through hole copper height.

Figure 6: Damage example – PTH trace disconnected from PTH barrel

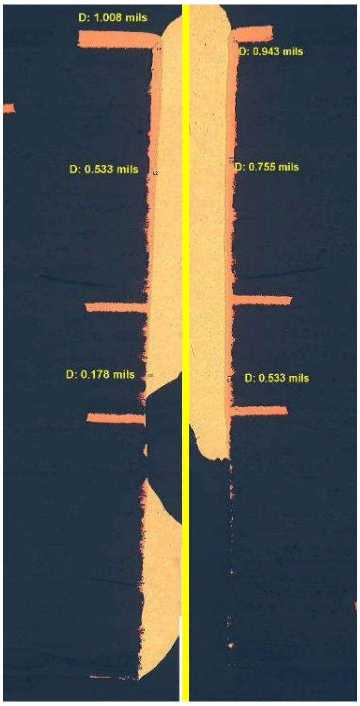


Figure 7: SN100C Cross-section of 0.036” PTH with 240 Seconds Exposure

As expected, the height of the plated through via also plays a role in the copper dissolution issue. Increasing the exposure time to the molten solder wave causes greater plated through via copper dissolution. Figure 8 illustrates how copper dissolution rates vary as a function of plated via measurement location along the length of the via. The bottom knee location had complete copper dissolution after approximately 100 seconds but the top knee location suffered only a reduction of 0.6 mils of copper after 240 seconds. This copper dissolution impact is important as product designers can make their designs inherently less vulnerable to the effects of copper dissolution by placing critical signal layers further from the printed wiring board lower half locations. Note that the dissolution rates shown in Figure 8 are specific to that particular via diameter and alloy. As will be shown in the subsequent sections of these reports, the smaller vias and other solder alloy showed significantly different rates of copper dissolution.

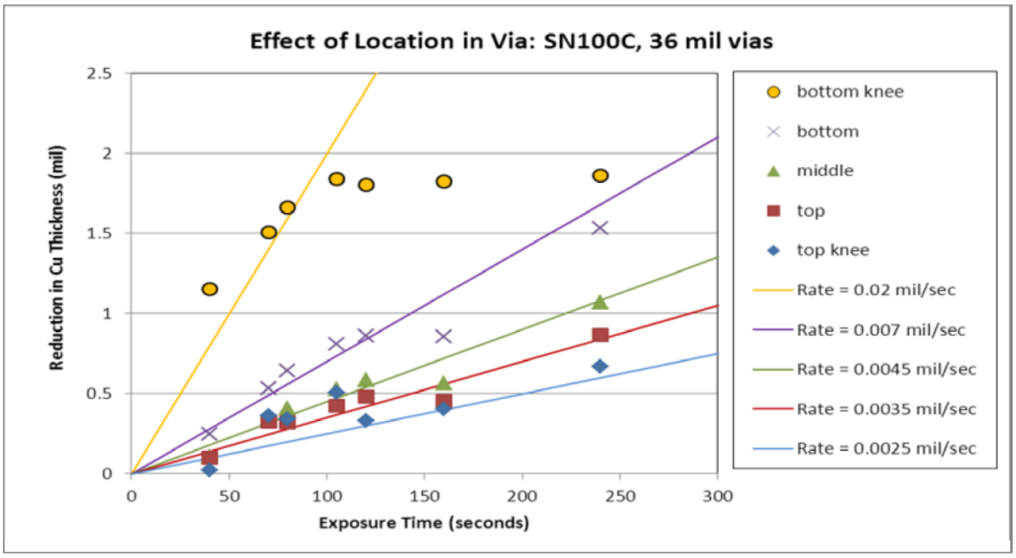


Figure 8: Copper Dissolution for SN100C Alloy Illustrating Impact of Location on Via Height

The dissolution rate of copper is a function of the specific solder alloy, via geometry, temperature and contact time during the PTH rework using a conventional mini-pot wave rework machine. Previous studies [2] [10] have shown that preheat temperature has an influence on dissolution. These studies indicated that using a higher preheat temperature helped to reduce the degree of Cu dissolution as it shortened the molten exposure time of the process, but not to a significant degree. For this study, the process temperatures were kept constant and the samples all started from room temperature.
Figure **9** illustrates the differences in copper dissolution rates for the SAC305 and SN100C alloys for the SMT QFP pad feature. The results shown in Figure 9 are in good agreement with the industry literature, with the SAC305 solder alloy having a higher copper dissolution rate than the SN100C solder alloy.

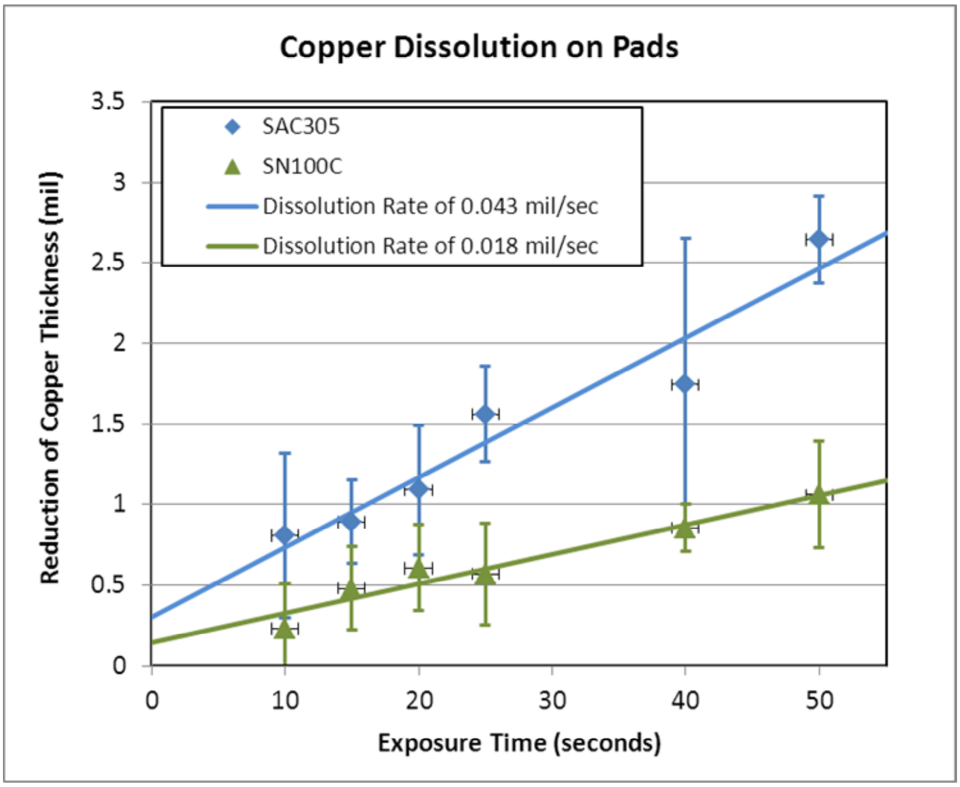


Figure 9: SAC305 and SN100C Copper Dissolution Results for SMT QFP

Figure 10 illustrates the differences in copper dissolution rates for the SAC305 and SN100C alloys for the PTH DIP via feature. This figure shows the rates of copper dissolution of the midpoint of the 36 mil and 15 mil vias for both types of solder alloys tested. Similarly to the SMT QFP pad results, the SAC305 solder alloy has a higher copper dissolution rate than the SN100C solder alloy for the 36 mil via size. The influence of the plated through via feature is illustrated in Figure 10 as the copper dissolution rates for the SAC305 and SN100C alloys are very similar for the 15 mil via size. The geometry of the 15 mil via reduces the molten solder contact exposure, which reduces the effective copper dissolution rates. This influence of the plated through via size can be potentially be used as a design advantage for copper dissolution concerns dependent upon necessary via functionality. For lead-free alloys, it has been shown that larger hole to pin ratios are required [11]**.** This larger hole requirement to enhance the via fill and resulting solder joint is inversely related to the copper dissolution interaction. Design considerations for lead-free products must take into account and balance the risks between copper dissolution and PTH solder hole fill.

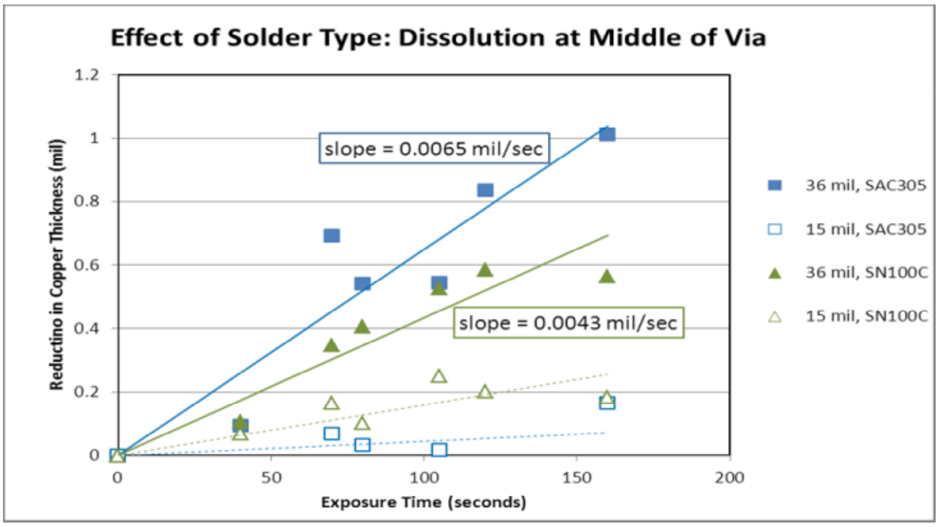


Figure 10: SAC305 and SN100C Copper Dissolution Results for PTH DIP at Middle Via Measurement Location

Figure 11 illustrates the slight differences in the average copper dissolution rates between the 36 mil and 15 mil via sizes for both solders that were evaluated. The error bars on this figure represent one standard deviation of the data.

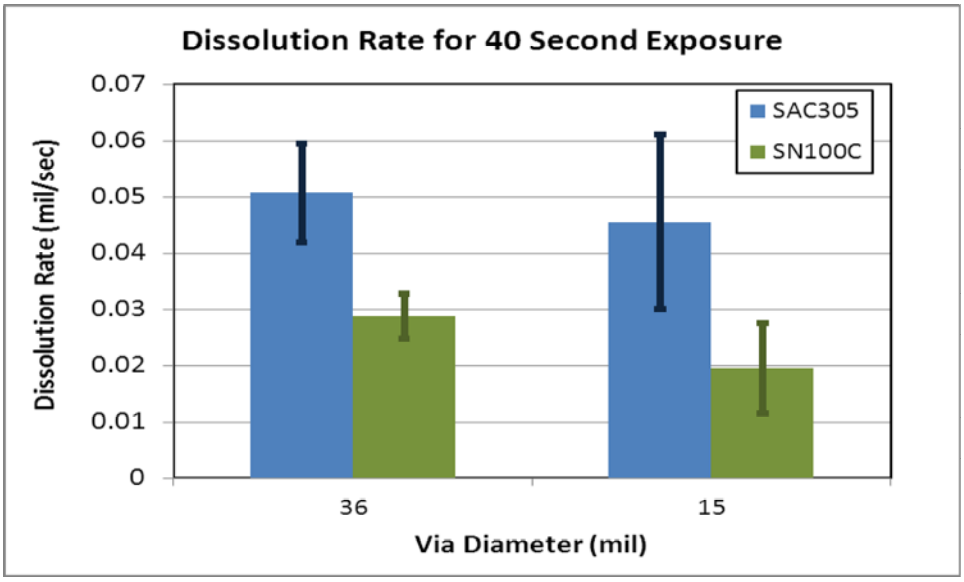


Figure 11: SAC305 and SN100C Copper Dissolution Rate Comparison for 40 Second Exposure

Since the dissolution of a plated through via knee is not readily detectible using typical assembly product stress screening, strict assembly process control limits are necessary to yield acceptable product reliability. Figure 12 shows soldering process windows for the SAC305 and SN100C solder alloys for two classes of electronic products. The dissolution rates used to define the process window values correlate to the test results plotted in Figure 11. The minimum copper plating thickness required for Class 3 products is 1 mil and for Class 2 products is 0.5 mils.

Based on the investigation data, the Figure 122 graph shows that the acceptable process window, i.e. cumulative wave solder exposure time is:

- ~77 seconds for SN100C and ~35 seconds for SAC305 in Class 3 products
- ~100 seconds for SN100C and ~44 seconds for SAC305 in Class 2 products

The selection of a particular lead-free soldering alloy significantly impacts the allowable assembly process window. Some product designs that had adequate process windows using tin/lead solder would be impossible to process using some lead-free solder alloys, since the time required to remove and replace a component would result in copper plating thickness falling below the required Class 2 or 3 minimum values.

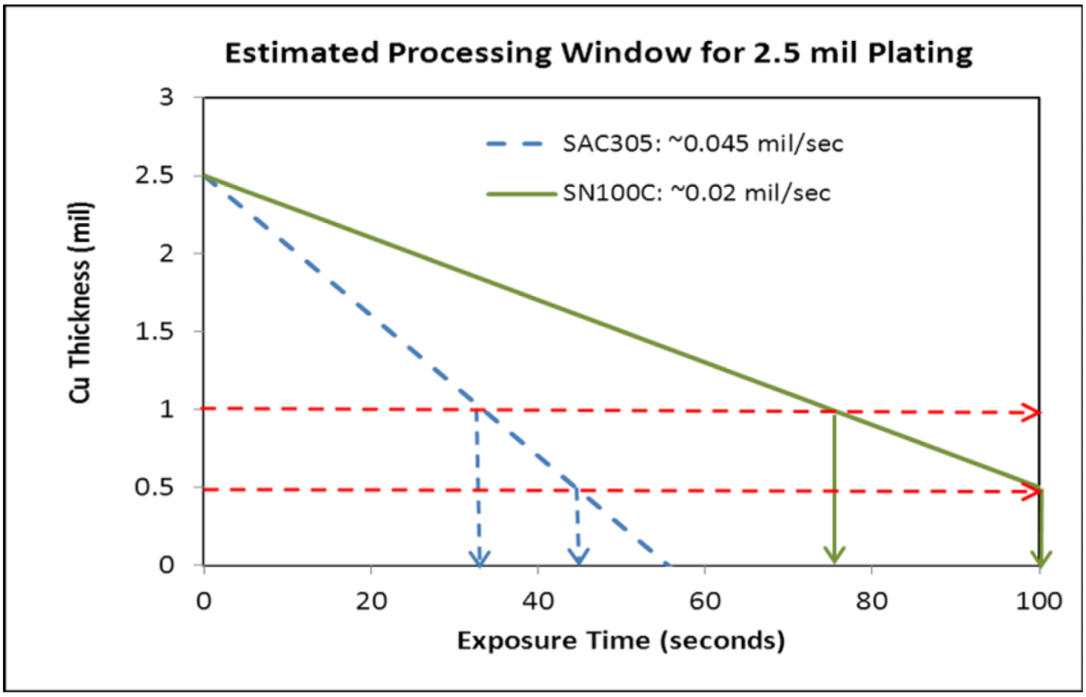


Figure 12: Mini Wave Soldering Processing Window Estimation

Figures 5 and 8 showed that copper is preferentially dissolved from the bottom of the hole towards the top. This is a result of the bottom side heating up first as it is exposed to the mini-wave rework pot. Thus the copper at the bottom of the via has a longer exposure to the copper dissolution reaction during a typical rework cycle. The impact to the PWB is that the bottom side catch pad (annular ring) and the knee of the PTH barrel will be the first to be impacted by the dissolution reaction. Traces that connect at the surface of the catch pad (annular ring) will experience greater dissolution, which may result in a broken connection by ring void at the PTH knee. This is a key visual indicator of copper dissolution and only x-ray can provide more detail on the internal PTH barrel condition.

The profile in Figure 13 shows how the hole typically heats up during the mini-pot wave rework cycle/exposure. This data shows that it requires 25 to 30 seconds for the top of the hole to reach the melting point.

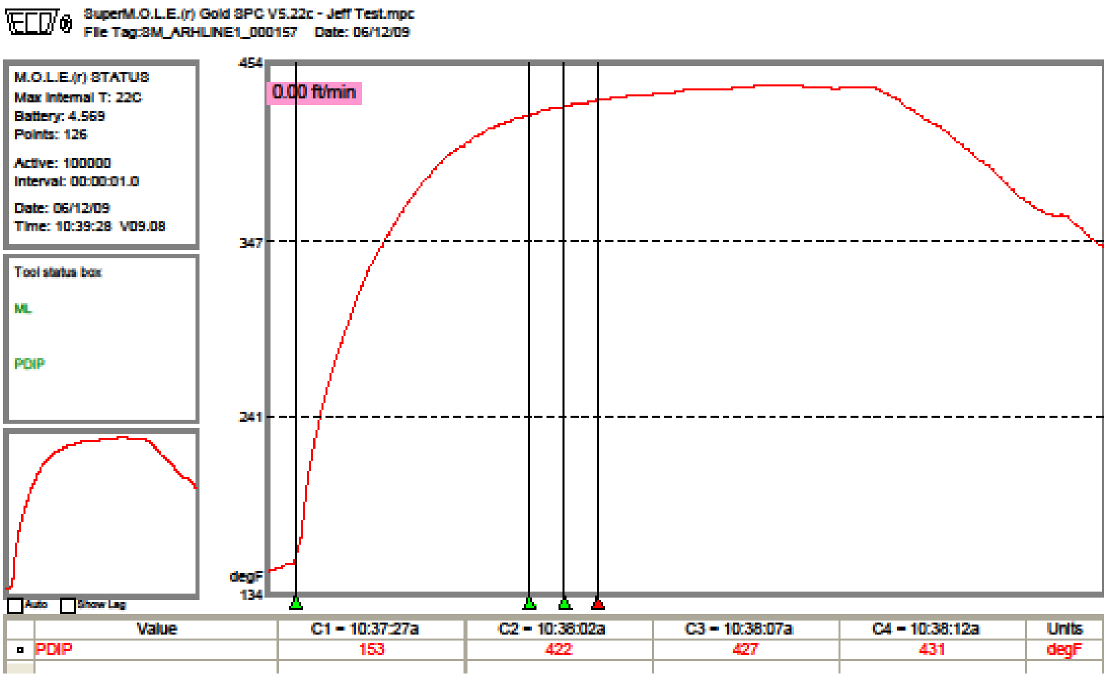


Figure 13: Rework Temperature Profile

Data and discussion for SMT pattern

The surface mount pads were also exposed to the mini-pot wave fountain to identify any drastic difference in copper dissolution between foil copper and plated copper. Normally, this exposure would not be part of a rework operation. Figure 14 shows the cross-section orientation for a SAC305 test coupon.

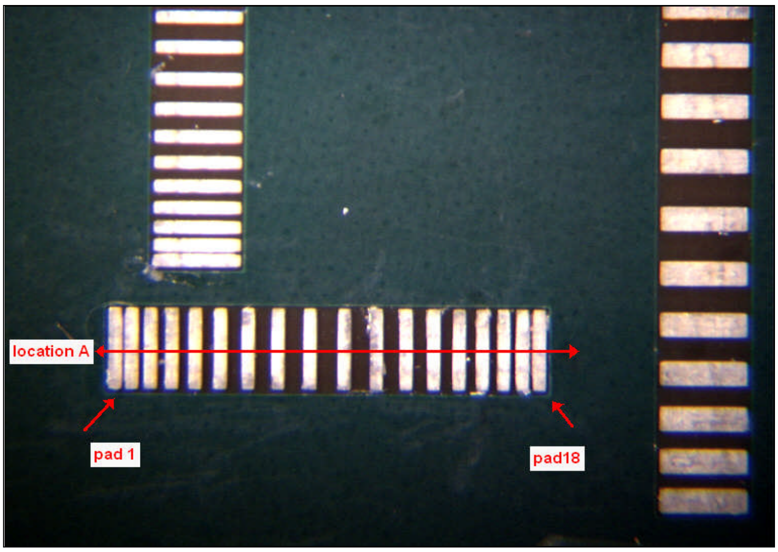


Figure 14: Celestica Location A Cross-section Location and Pad Number

Figure 15 shows the sequence of pad foil copper dissolution over a period of time. The slope, i.e. the copper dissolution rate, was found to be approximately 0.04 mils/second. This is very similar to the rate of copper dissolution determined at the knee of the DIP PTH for SAC305.

Sample A166, pad 1, 200 X
10 sec exposure

Sample A182, pad 1, 200x
15 sec exposure

Sample A186, pad 1, 200x
20 sec exposure

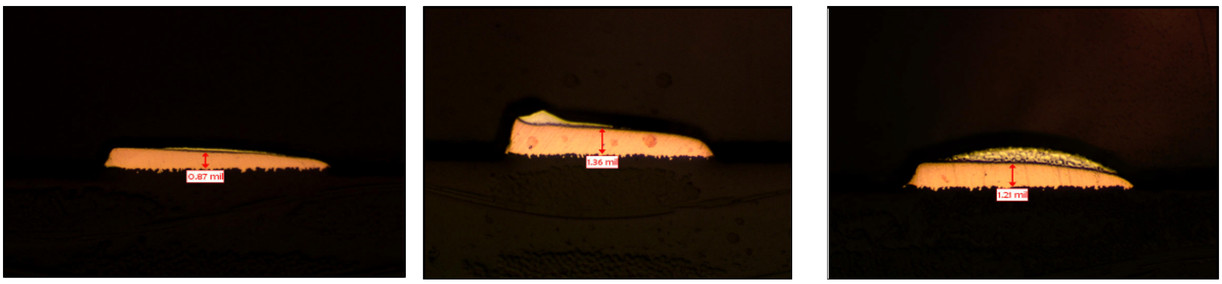
Sample A42, pad 18, 200x
25 sec exposure

Sample A171, pad 18, 200x
40 sec exposure

Sample A176, pad 18, 200x
50 sec exposure

Figure 15: Sequence of Pad Copper Dissolution by Exposure Time

Figure 16 shows an example of the copper dissolution variance within a specific exposure time. The dynamic nature of the molten wave as it interacts with the plated through via or surface mount pad results in variation of remaining copper plating thickness, despite using tightly controlled test parameters and procedures. It should be noted that the copper dissolution rate for the SMT pads is not much different that of the PTH. This indicates that foil copper dissolves at nearly the same rate as the plated PTH copper.



Sample A185, pad 9, 200x

Sample A186, pad 9, 200x

Sample A187, pad 9, 200x

Figure 16: Illustration of Copper Dissolution Rate Variance for A Specific Exposure Time

Figure 17 illustrates a temperature profile that shows the SMT QFP pads reaching reflow temperature within 5 seconds. The copper is exposed to molten alloy from the moment of contact, so the effect of the copper dissolution reaction is more damaging than in a plated PTH barrel. Typically, the surface mount pads would start with a lower copper thickness than those of a PTH barrel on the same circuit card assembly (depending on whether it is pattern plated or panel plated) so those features would be more severely impacted if they were in the vicinity of a PTH connection that is exposed to the rework process.

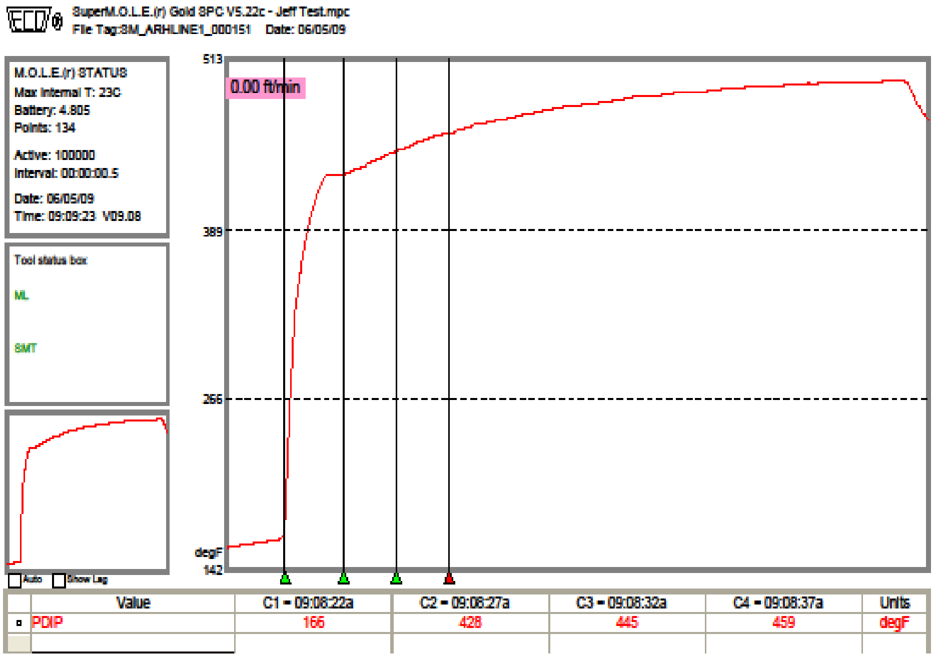


Figure 17: SMT QFP Pad Thermal Profile

Inspection Criteria – Visual Indicators of Copper Dissolution

Visual inspection confirmed that the PTH catch pad and the knee of the PTH solder joint were the most susceptible locations for copper dissolution. The rate of copper dissolution is greater at this surface as compared to the inner barrel wall. Fillets at the knee may indicate a discontinuity at the location and may be a visual indicator for possible partial void/disconnection location. These visual indicators, illustrated in Figure 18 can be used by the operator to determine if there is an out-of-control process.

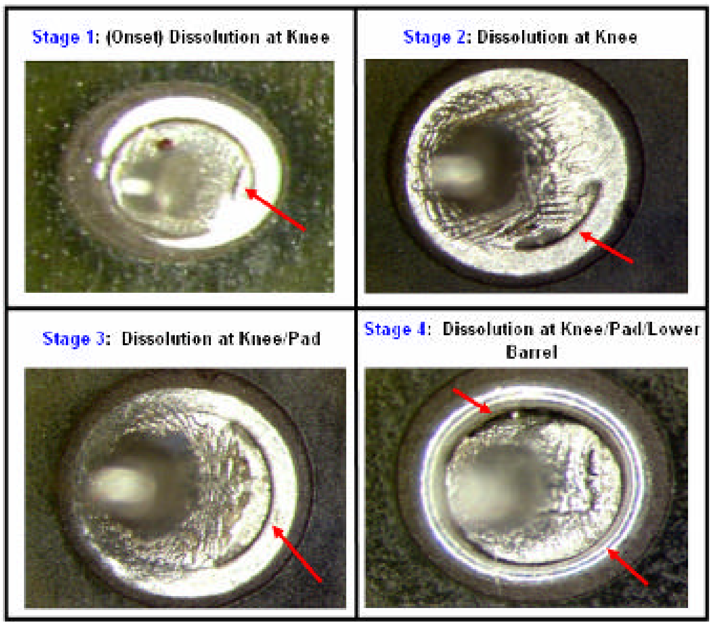


Figure 18: Visual Indicators of Copper Dissolution [2]: Knee- Pad- Barrel for Location of Copper Reduction Sequence

Kinetics of Copper Dissolution

Celestica and Rockwell Collins have conducted past investigations to understand copper dissolution in a lead-free soldering process [11] [12]. The dissolution of copper by a tin/lead solder alloy is not a "new" topic and is fairly well documented. The following information details the basics of copper dissolution. The copper dissolution process itself can be considered a result of the following mechanisms [3]:

(1) Departure of atoms of the solid surface and
(2) Diffusion into the molten solder

Diffusion controlled processes result in a uniform attack while interface controlled reactions may be recognized by preferential etching of grain boundaries. In this study, smooth copper/intermetallic interface without any sign of grain boundary attack was detected. The mechanisms occur in series and the slowest one determines the overall kinetics of the process. The most general dissolution rate equation is shown below [4]:

$C = Cs\ (1\text{-}exp^{(-K\ (A/V)\ t)})$,

where C is the solute concentration at time t, K is the solution rate constant and V is the volume of liquid. This equation can be applied for diffusion controlled or interface controlled processes. The solution rate constant K is D/d for the case of diffusion control, where D is the diffusion coefficient in liquid and d is the thickness of the effective concentration boundary layer. In general, the boundary layer thickness is less than 0.1mm. This boundary layer is a layer of liquid existing immediately adjacent to the solid copper interface/intermetallic layer (Figure 19). The copper concentration gradient exists within this layer. During the diffusion controlled process, the liquid boundary layer that is formed during the solder fountain rework is an important feature of copper dissolution.

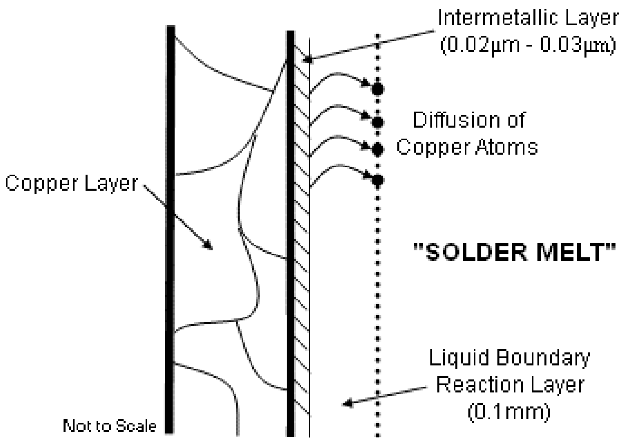


Figure 19: Departure and Diffusion of Copper Atoms into Solder Melt (Kinetics of Copper Dissolution)

<u>Sn-Pb and Sn-Ag-Copper and Sn-Copper Based Alloys</u>

It has been recognized that it is the Sn component of most solders that reacts with the copper substrate [5]. In the case of Sn-Pb solders, only the tin components react, since copper is nearly insoluble in liquid lead at soldering temperatures and forms no intermetallic compounds with it. Therefore, Sn-rich solders dissolve more copper than eutectic Sn-Pb solder. With increasing copper concentration in the solder, the rate of dissolution decreases because of the concentration gradient reduction. Thus, solders with 0.7% copper remove less copper from the plating layer than solders with 0.5% copper. The thickness of this liquid diffusion boundary layer is a function of the physical properties, the velocity of the solution and the diffusion coefficient. The dissolution rate increases with increasing peripheral velocity, which is relevant to the fountain rework situation. [9] [10]

The SAC305 alloy test results shown in
Figure **20** are from the solder pot post testing. The limits are all within IPC industry standard levels.

TEST REPORT
A I M
AIM REF. #: 0907-093
DATE: 7/22/2009
ELEMENT RESULT (%)
PRODUCT: SAC Alloy
CUSTOMER: Celestica -Mn
CUST. REF. #: LF1
LIMITS (%)
8654
(Ag) SILVER 3.27 4.25
(Al) ALUMINIUM <0.001 0.006
(As) ARSENIC <0.007 0.03
(Au) GOLD <0.001 0.4
(Bi) BISMUTH 0.006 0.1
(Cd) CADMIUM <0.001 0.005
(Copper) COPPER 0.521 1
(Fe) IRON 0.002 0.04
(Ni) NICKEL 0.003 0.05
(Pb) LEAD 0.022 0.1
(Sb) ANTIMONY 0.017 0.2
(Sn) TIN Bal.
(Zn) ZINC <0.001 0.006

Figure 20: SAC305 Solder Pot Analysis Results

Copper Dissolution Impact on Assembly Practices:

The impact of solder alloy copper dissolution on assembly procedures and practices is significant. The process window for the removal and repair of a lead-free plated through hole components is significantly smaller than the process window used for tin/lead solder alloys. A complicating factor is that a copper dissolution defect is not readily detectible by visual or functional test protocols. The solder filled plated through hole has an acceptable functional response due to the solder providing signal continuity. However, the reality of the situation is that once the solder cracks, the lack of copper plating results in the loss of electrical continuity. The following sections detail several aspects of copper dissolution on assembly procedures/practices:

- <u>The plated through hole component rework/repair procedure</u>
  Traditional tin/lead solder alloy provided a very large rework/repair process window with little concern for copper dissolution of the copper plating and more emphasis was placed on potential printed wiring board laminate defects such as delamination or component damage due to total heat exposure duration. The impact of using either the SAC305 or SN100C solder alloys is that the maximum exposure time to a dynamic solder wave is approximately 25 seconds. This time constraint can be especially problematic for heavy copper /thermally loaded printed wiring assemblies by severely limiting the exposure time and allowable additional exposures. The use of alternative component removal methodologies such as hot air and/or rework attachment using a selective solder process should be considered as possible substitutive process methodologies for the removal of components to minimize the impact of copper dissolution.

- <u>The use of alternative printed wiring board surface finishes</u>
  The characteristics of some printed wiring assemblies, such as the number of copper layers and/or how the plated through holes are connected, may make lead-free solder alloy rework/repair unachievable. Consideration of, and risk analysis for, the use of alternative printed wiring board surface finish such as electroless nickel/immersion gold (ENIG) that are plated directly on copper with no intermediary plating layer such as nickel may be necessary. Figure 21 illustrates the difference between two surface finishes. ENIG nickel plating on the left hand side show that the nickel plating protects 0.0015" of copper plating from copper dissolution even after 60 seconds exposure in a SAC305 flowing solder pot. The immersion tin surface finish shown on the right hand side allowed nearly completed dissolution of the copper plating at the knee of the plated through hole for the same 60 second exposure time.

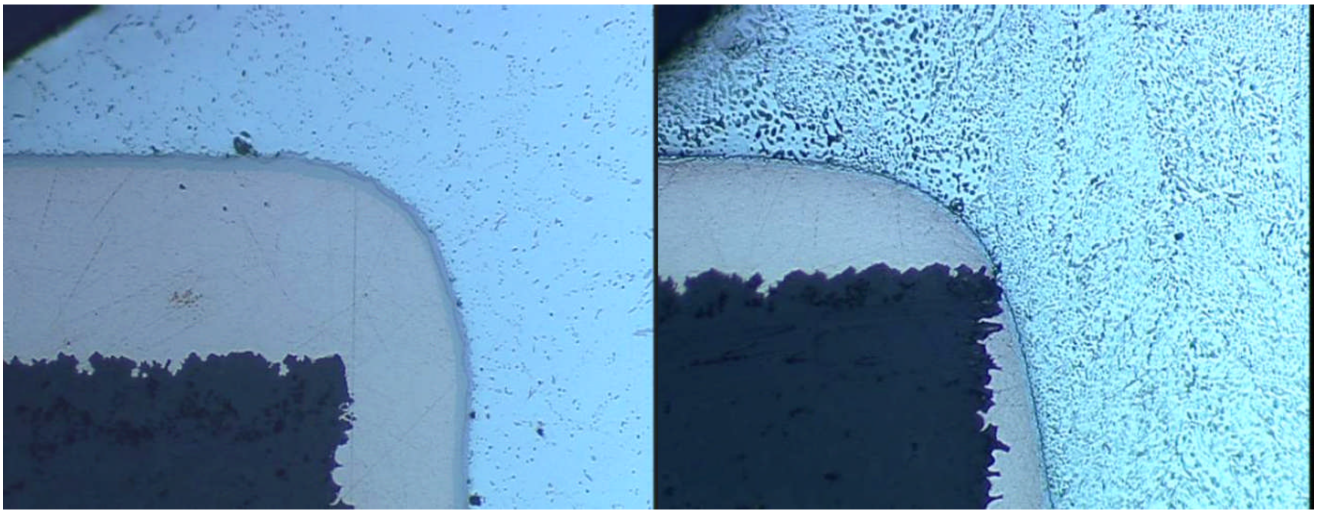


Figure 21: Impact of PWB Surface Finish on Copper Dissolution; Left - ENIG, Right - Immersion Tin

Conclusions/Summary

A number of issues related to copper dissolution should be addressed for products to making the transition to lead-free assembly. These include:

- The amount of initial copper plated in the PTH hole may need to be increased to establish a greater margin of safety. The current requirement for 1 mil copper plating minimum may need to be increased to as high as 2.0 mils to provide this margin.
- A resultant minimum copper thickness after rework process may need to be specified and validation methods to ensure compliance would need to be established.
- Alloy selection for rework may be different than for primary attach depending on the expected number of rework cycle requirements for the given product lifetime. Some initial studies have indicated that mixing various Pb-free alloys will not degrade solder joint quality or solder joint reliability. [1]
- Copper dissolution rates vary somewhat with the PTH diameter. This study included only two hole sizes: 0.036" and 0.015". The smaller hole may have impact on material flow up and down the PTH barrel, which affects the copper dissolution rate. Product design consideration may require some additional testing to validate product parameters and associated process requirements. [11]
- Rework locations need to be identified by reference designator.
- Control and recording of rework exposure time may also be required to ensure the connection will meet lifetime requirements of the product.
- Tighter controls on solder pot contaminant levels and maintenance of pot composition may be required to reduce variance of the copper dissolution effect during rework operations.
- Consideration for larger component sizes with regard to nozzle design and alloy flow during the rework procedure may be necessary. [9]

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