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# HAVE HIGH Cu DISSOLUTION RATES OF SAC305/405 ALLOYS FORCED A CHANGE IN THE LEAD FREE ALLOY USED DURING PTH PROCESSES?

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## ABSTRACT

To date, the majority of the Electronics Manufacturing industry has implemented either SAC305 or 405 alloys to manufacture Pb-free (E.U. RoHS, compliant) products, for both the SMT and PTH card assembly processes. This original alloy composition choice, dating back to 1999, was based on early research into the metallurgy and reliability of the alloy/s and agreement amongst top companies involved in iNEMI, JEITA and within the European Union. A recent shift towards SAC305 has recently been observed within the industry due to its lower cost when compared to SAC405 based on lower silver content. Historically, reliability assessment efforts have focused on SMT solder joint connections as PTH solder joint connections were not typically a reliability concern due to their construction. Conceptually, it is easier from a process and supply chain point of view to use a single Pb-free alloy for both the SMT and PTH attach process. However, issues relating to high rates of copper (Cu) dissolution occurring during the PTH rework process using either SAC305 or 405 alloys may force a change in this concept.

The high Cu dissolution rates experienced when using SAC305/405 may dictate a change in the Pb-free alloy used during the PTH rework process, in order for typical methods of rework (i.e. solder fountain) to continue to be used. However, making a change in the Pb-free alloy used for only the PTH rework process itself creates new questions which would need to be answered. For instance, what is the impact of reworking a SAC305/405 assembled connector using an alternate Pb-free alloy? Is changing the Pb-free alloy used within the primary attach process to match the PTH rework alloy the right solution? This leads to further questions relating to process controls and reliability of a final “mixed” Pb-free joint as well as the “pure” alternative Pb-free alloy selected which would need to be addressed.

This paper discusses the work performed studying and comparing the Cu dissolution rates of various Pb-free alloys available on the market today. Although the use of a PCB with a nickel plated layer can reduce the occurrence of Cu dissolution, all experiments in this study were performed on

an OSP finished board. Finishes such as OSP which do not have a nickel later represent the worst case scenario with respect to Cu dissolution. An OEM server product was used as the test vehicle throughout this study. A total of six Pb-free alloys and a eutectic tin/lead (Sn-Pb) control alloy were included in the evaluation. Specifically, two binary eutectic and four ternary “near eutectic” Pb-free alloys were included. Each of the “alternative Pb-free alloys” studied include varying levels of certain elemental additives. Common additives included in some of these alloys are, nickel (Ni), germanium (Ge), bismuth (Bi) and antimony (Sb). This paper also includes a brief metallurgical analysis into the effects of adding each of these above additives. In addition, both time zero analysis and ATC (0-100°C) thermal reliability analysis of the Sn-Cu + Ni solder vs. SAC405 will also be discussed. Finally, the manufacturing impact when altering the Pb-free PTH alloy will be briefly discussed, including process control, contamination, cost and supply chain considerations.

There is enough data to indicate that several alternative Pb-free alloys available on the market today are suitable replacements to SAC305/405 for PTH solder fountain rework, allowing up to a 2X rework process. In addition, the cost of these alloys warrants further study into also replacing the wave solder alloy as a cost reduction to SAC305/405.

Keywords: Cu dissolution, Pb-free, process window, PTH rework, PTH primary attach

## INTRODUCTION

There is no doubt that any EMS company who has made the transition over to Pb-free assembly, and has attempted to rework PTH connectors using conventional equipment with either SAC305 or 405 alloys would have experienced some degree of Cu dissolution. Depending on the size and complexity of the connector and PCB itself, the extent of dissolution would have ranged from either a slight loss of the barrel knee and annular ring edges to a complete loss of the pad surface, barrel knee and portions of the barrel wall on numerous barrel locations of the reworked connector.

This occurrence of Cu dissolution during PTH rework is not a new phenomenon. In some cases, high degrees of Cu dissolution occurred under Sn-Pb conditions when reworking larger, more thermally massive PCBs which required longer contact times (i.e. server type product). In some instances, a “low-melt” alloy was incorporated into the Sn-Pb process in order to allow the longer contact times required for 2X rework<sup>1,2</sup>. This however, was only required on an extremely small percentage of card types. The majority of PTH reworks were capable of using the one alloy type (i.e. eutectic 63Sn-37Pb). However, now with having to use Pb-free alloys such as SAC305 or 405 this issue relates to the majority of product types – regardless of size and complexity. The main reasons for this increase in Cu dissolution using SAC305/405 are due to the increased operating temperatures, along with the change in the alloy composition itself. Primarily, it is the increase in tin content (%Sn) which causes higher rates of Cu dissolution. Aside from incorporating other techniques to attempt to reduce the degree of Cu dissolution, such as methods of reducing contact time using barrel cleaning techniques as well as methods of reducing flow rates, it is clear that a change in Pb-free alloy is the main solution required in order to establish a safe PTH rework process window, which the industry has been accustomed to when using Sn-Pb alloy.

There are a handful of alternative Pb-free alloys available on the market today which are variations of Sn-Ag-Cu or Sn-Cu based alloys which have varying degrees of elemental additives such as nickel (Ni), germanium (Ge), bismuth (Bi), antimony (Sb) + others. These additives add certain properties which help in controlling the grain structure which acts to reduce the degree of Cu dissolution as well as offer other soldering benefits. The specific alloys included in this study, along with their respective melting ranges are listed in Table 1. The impact of these additives from a metallurgical point of view will be briefly discussed.

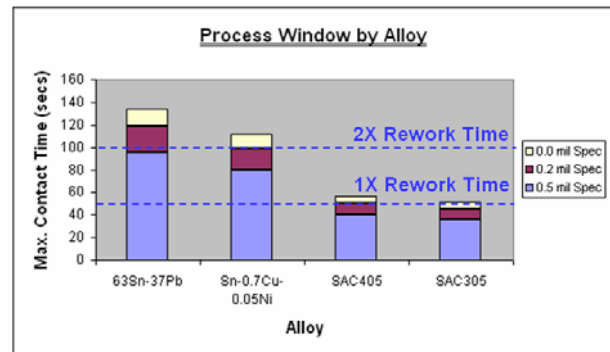
**Table 1.** Alloy Composition and Melting Range

ALLOYS		MELTING RANGE
63Sn-37Pb	(Sn-Pb)	183°C
95.5Sn-3.8Ag-0.7Cu	(SAC405)	217° to 220°C
96.5Sn-3.0Ag-0.5Cu	(SAC305)	217° to 224°C
99.1Sn-0.7Cu-0.05Ni-( $<0.01$ )Ge <sup>1</sup>	(Sn-Cu + Ni)	227°C
98.6Sn-0.3Ag-0.7Cu-Bi-X-Y <sup>2</sup>	(Sn-Ag-Cu + Bi)	217° to 228°C
96.0Sn-2.5Ag-0.8Cu-0.5Sb	(Sn-Ag-Cu + Sb)	217° to 219°C
99.1Sn-0.7Cu-X-Y	(Sn-Cu + X)	227°C
1. U.S. Patent # 6180055		2. Patent # PCT/GB2005/004609

## BACKGROUND

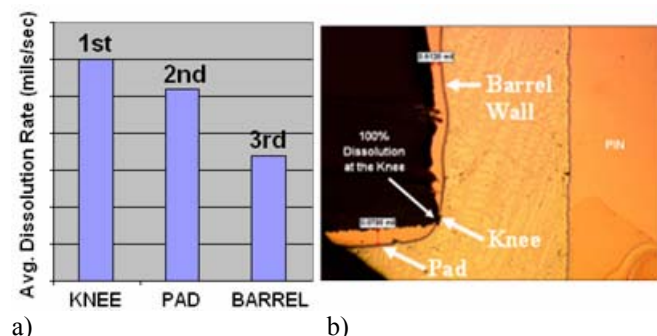
To date, previous studies on the phenomenon of Cu dissolution have resulted in several key outcomes. Firstly, the industry will likely be forced to move away from using SAC305/405 alloys during PTH processes<sup>3,4</sup>. The main reason for this is based on the high Cu dissolution rates of these alloys, having a direct impact during the PTH rework process. This is a concern, especially for high reliability, long life products which may require multiple reworks during their lifetime. It has been shown that both SAC305

and 405 alloys have Cu dissolution rates which are 2X higher when compared to a Sn-Cu + Ni doped alloy and a conventional Sn-Pb eutectic alloy. The calculated Cu dissolution rates are directly correlated to the allowable PTH rework process window. It can be seen that significant improvements to the allowable process window are made when using an alternative Pb-free alloy which offers lower rates of Cu dissolution as shown in Figure 1.



**Figure 1.** PTH Process Window by Alloy

The second conclusion was that Cu dissolution rates will vary from barrel-to-barrel across a connector and will even vary within a single barrel based on geometry (Figure 2 a,b). Specifically, the knee of the PTH barrel will dissolve at a faster rate as compared to the annular ring and/or barrel wall<sup>5</sup>. This is explained by atomic diffusion theory correlating the effects of surface geometry on the rate of atomic diffusion, as well as proximity to the solder flow. The main reason for the variance across a connector has been linked to flow rate. Typical flow-well design utilizes a single central opening through which solder can flow. This design point often results in higher dissolution rates within center barrels of a connector rework location. Center pins are often subjected to turbulent solder flow, while edge pins are subjected to laminar flow. Modifications in flow-well design have proven effective in reducing solder turbulence, resulting in reduced Cu dissolution rates during solder fountain rework<sup>6</sup>.



**Figure 2.** a) Cu dissolution rates by barrel geometry ; b) X-section showing 100% Cu dissolution at the knee location.

## METALLURGICAL THEORY

All of the “alternative Pb-free alloys” included in this study are primarily Sn-Ag-Cu or Sn-Cu based alloys with some controlled levels of additives. It is the addition of these

additives which help to control the final grain structure thus improving final joint appearance, wetting, and flow characteristics. Resultant effects include improved barrel fill and reduced Cu dissolution. The type, wt% and combination of the base elements and additives all have an impact on controlling the above properties. This section will provide a summary on the impact of each of the common additives, specifically on effecting Cu dissolution from a metallurgical point of view.

### Kinetics of Cu Dissolution

Before being able to discuss the impact of each of the additives on Cu dissolution, the basic mechanisms behind how Cu dissolution occurs need to be explained.

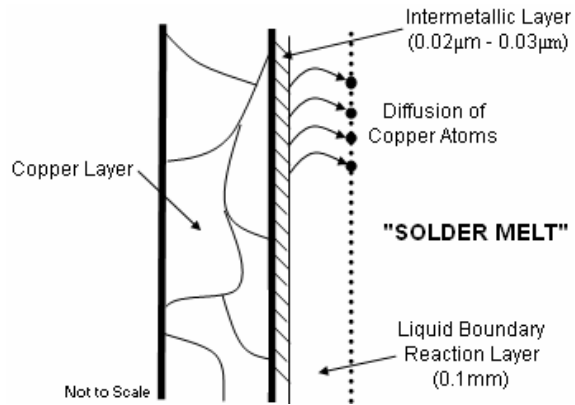
The Cu dissolution process itself can be considered as occurring by the following mechanisms<sup>7</sup>:

- (1) Departure of atoms of the solid surface and
- (2) Diffusion into the solder melt.

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 signs of grain boundary attack was detected. The mechanisms themselves occur in series and the slowest one determines the overall kinetics of the process. The most general dissolution rate equation is shown below<sup>8</sup>:

$$C = C_s(1 - \exp(-K(A/V)t))$$

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  $D/\delta$  for the case of diffusion control, where D is the diffusion coefficient in liquid and  $\delta$  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 (Cu) interface/intermetallic layer (Figure 3). The Cu concentration gradient exists within this layer. During the diffusion controlled process the liquid boundary layer which is formed during the solder fountain rework is an important feature of Cu dissolution.



**Figure 3.** Departure and Diffusion of Cu Atoms into Solder Melt (Kinetics of Cu Dissolution)

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. Other influences in reducing Cu dissolution would be based on the type of additive present in the bulk solder. The exact influence of each will be discussed below.

### Sn-Pb and Sn-Ag-Cu and Sn-Cu Based Alloys

It has been found that it is the Sn component of most solders that reacts with the copper substrate<sup>9</sup>. In the case of Sn-Pb solders, only the Sn components react, since Cu is nearly insoluble in liquid Pb at soldering temperatures and forms no intermetallic compounds with it. Therefore, the Sn-rich solders dissolve more Cu 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% Cu remove less copper from the plating layer than solders with 0.5% Cu. Therefore, based on this, the Cu dissolution rates of the SAC305 alloy (0.5%Cu) should be greater than that of the SAC405 alloy (0.7%Cu). This will be further illustrated in the results section.

### Effect of Additives

An effect of a reactive third and fourth component within a binary and ternary based alloy respectively is not properly understood yet and cannot be predicted without experimentation under different conditions. Below is brief summary of the expected reaction of common additives specifically with respect to controlling Cu dissolution.

1. Some components such as Sb and Bi may dilute the Sn-rich solder and reduce Cu dissolution in molten solder. Typically these elements improve solder grain structure, strength and/or ductility. However they are prone to defects such as fillet lifting and contamination issues.
2. Some metals that react with Sn may increase the effective Cu concentration in the bulk molten solder and slow down the Cu dissolution rate by reducing the

concentration gradient. The Ni additive substitutes Cu in  $Cu_6Sn_5$  particles forming a complex  $(Cu,Ni)_6Sn_5$  compound. The ternary  $Cu_xNi_ySn_z$  formation was reported as well<sup>10</sup>. For better understanding of the Ni influence on the Cu dissolution rate the next level of complexity of the dissolution should be described. At the interface of copper and molten solder an intermetallic layer is formed, which grows at the copper side and at the same time dissolves at the solder side<sup>11,12</sup>. This intermetallic layer (Figure 3) is very small about  $0.02 - 0.03\mu m$ <sup>13</sup>. The Ni component is concentrated in the intermetallic layer. In this case small quantities can have major effect on the concentration gradient within the Cu layer. This gradient significantly slows down the dissolution of Cu.

- When an additive reacts with dissolving Cu, the effective concentration of Cu is lowered and the dissolution rate is consequently raised. The oxygen component may cause the Cu dissolution rate to increase, when the molten solder is exposed to air. If species such as Ge (an antioxidant) which reacts with oxygen is present the dissolution rate will go down.

### TEST VEHICLE

The test vehicle (Figure 4) selected was a current OEM product card. It was selected due to its thermal nature, in order to characterize Cu dissolution on a large, thermally massive PCB. The dimensions are 226mm x 493mm (8.9" x 19.4"), with a thickness of 2.4mm (0.096"). It consists of 24 layers which are 0.5 or 1 ounce copper plating, with multiple ground connections and has an OSP surface finish, with a high Tg FR-4 laminate. The board is populated with 32 in-line DIMM connectors.

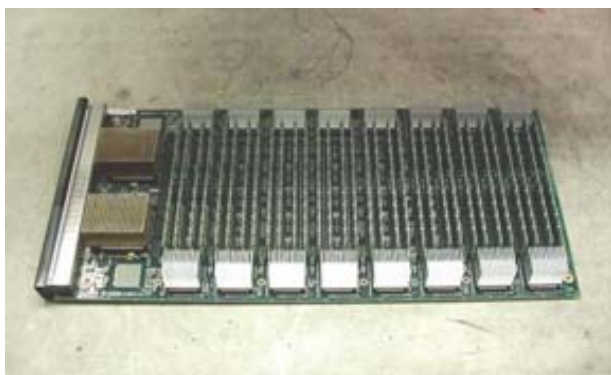


Figure 4. Test Vehicle (High Thermal Mass)

### EXPERIMENTAL PROCEDURE

The Cu dissolution DOE matrix followed is shown in Table 2. The testing of each alloy was separated into two experimental groupings (Exp# 1 and 2) with two test vehicles used.

Table 2. Cu Dissolution DOE Matrix

Exp. #	ALLOY	Contact Time Replicates (secs)					
		1	2	3	4	5	6
1-1	Sn-Pb	30	30	30	30	30	30
		50	50	50	50	50	50
1-2	SAC405	30	30	30	30	30	30
		50	50	50	50	50	50
1-3	SAC305	30	30	30	30	30	30
		50	50	50	50	50	50
1-4	Sn-Cu + Ni (1)	30	30	30	30	30	30
		50	50	50	50	50	50
2-1	Sn-Ag-Cu + Bi	30	30	30	30	30	30
		50	50	50	50	50	50
2-2	Sn-Ag-Cu + Sb	30	30	30	30	30	30
		50	50	50	50	50	50
2-3	Sn-Cu + X/Y	30	30	30	30	30	30
		50	50	50	50	50	50
2-4	Sn-Cu + Ni (2)	30	30	30	30	30	30
		50	50	50	50	50	50
DOE RUNS		16	16	16	16	16	16
TOTAL DOE RUNS		96					

The first experimental grouping (1-1 to 1-4) included three different Pb-free alloys (Sn-Cu + Ni, SAC305 and SAC405) along with a eutectic Sn-Pb control cell. The second grouping of alloys (2-1 to 2-4), included four Pb-free alloys a 6-part Sn-Ag-Cu alloy with Bi + "other" additives, a Sn-Ag-Cu with an Sb additive, a Sn-Cu alloy with two minor additives (1.0% each) as well as a repeat of the Sn-Cu alloy with Ni and Ge (<0.01%) additive. Each sample was exposed to two different contact times (30, 50 seconds) using each alloy.

The primary factors that were varied in the experiments were solder alloy and contact time. All other potential variables were set as constants, such as flux type, equipment type, preheat method and preheat time. However, as each alloy has a different melting temperature, the pot temperature was also changed to ensure constant superheat (Table 3). This is important as alloy temperature does have an impact on dissolution rates. Keeping each alloy's superheat consistent was an attempt to remove the variability caused by the differing melting temperatures of each alloy.

Table 3. Alloy Temperature Details

ALLOY	Melting Temp	Pot Temp	Super Heat
Sn-Pb	183	233	50
SAC405	217	267	50
SAC305	217	267	50
Sn-Cu + Ni	227	277	50
Sn-Ag-Cu + Bi	217	267	50
Sn-Ag-Cu + Sb	217	267	50
Sn-Cu + X/Y	227	277	50

\*temps in degreesC

In each group, a bare board was used for the experiment, separating individual DIMM locations into the DOE samples (Figure 5). The total sample size including all seven alloys was 96 (48 samples per board), with each sample consisting of approximately 14 barrel locations.

This would equate to 28 separate Cu thickness measurements taken per sample.

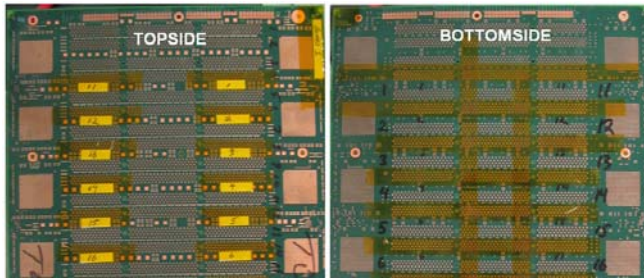


Figure 5. Sample Preparation

Each DOE sample was cross-sectioned along the entire length of the sample at a middle row and Cu thickness measurements taken. Cu thickness measurements were focused solely at the knee location (Figure 6). In absence of a current IPC industry specification for remaining Cu plating thickness after rework, an OEM specification of 0.5 mils of remaining Cu plating was used<sup>14</sup>.

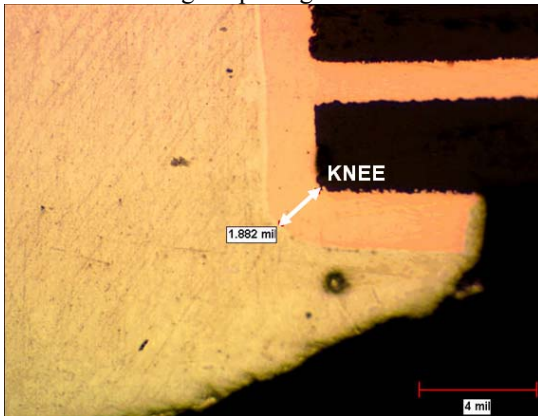


Figure 6. Cu Thickness Measurement Locations

## EXPERIMENTAL RESULTS

The statistical results indicate that both contact time as well as alloy type have a significant impact on the rate of Cu dissolution (Table 4).

Table 4. ANOVA Statistical Results Showing Significance of Contact Time and Alloy

Analysis of Variance for min_knee (mils), using Adjusted SS for Tests						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Contact Time (secs)	1	1.70428	1.61816	1.61816	28.10	0.000
Alloy Coded	6	6.08388	5.98639	0.99773	17.33	0.000
Contact Time (secs)*Alloy Coded	6	0.56246	0.56246	0.09374	1.63	0.164
Error	41	2.36102	2.36102	0.05759		
Total	54	10.71163				

The interaction plot (Figure 7), illustrates the Cu dissolution results of each alloy at both 30 and 50 second exposure times. The values on the y-axis are the measured remaining Cu thickness of the knee plating after a 30 and 50 second exposure to molten solder (x-axis). The alternative Pb-free alloys have been coded (Alloy A, B, C and D) with the results of SAC305, 405 as well as the Sn-Pb control cell identified in the chart.

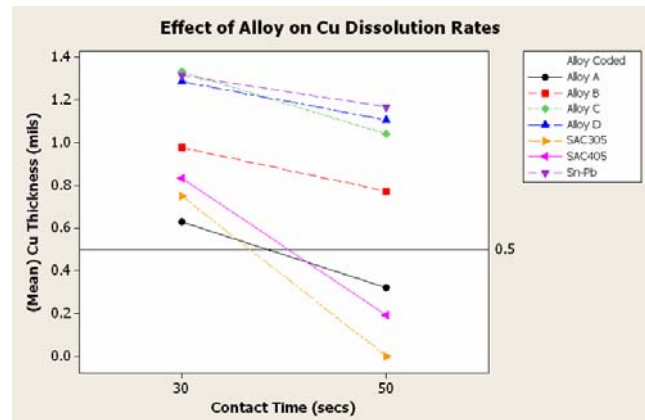
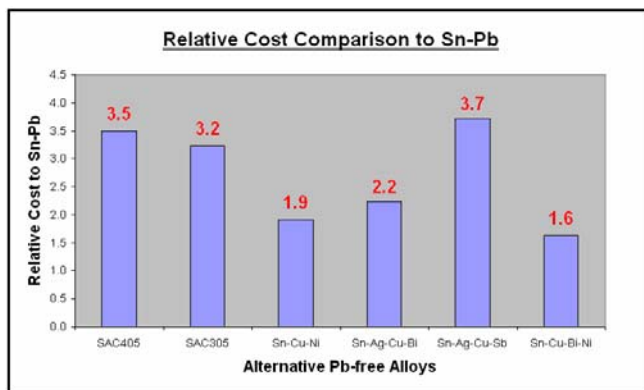


Figure 7. Interaction Plot Results – Effect of Alloy on Cu Dissolution Rates

The results show that two of the alternative Pb-free alloys performed the best with respect to the rate of Cu dissolution occurring. Specifically, Alloy C and D results are comparable to those of the Sn-Pb control cell. In addition, Alloy B's result also showed a statistically significant difference from the performance of SAC305/405 alloys and although showing poorer results, it had no statistical difference compared to Alloys C, D and the Sn-Pb cell. Although it had a similar slope to the other alternative Pb-free alloys, Alloy A showed a slightly higher occurrence of Cu dissolution at the exposure times of 30 and 50 seconds. Alloy A has a statistically similar rate of dissolution compared to the SAC305/405 alloys. It can be seen from Figure 7 that Alloy A's results drops below the specification limit of 0.5 mils of remaining Cu plating at approximately 40 seconds, which is a concern.

As the Pb-free PTH process window is strongly dependant on total cumulative exposure to solder, the final Cu dissolution rates calculated can be correlated to a maximum expected allowable process window for each alloy studied. Figure 8 illustrates each alloy's process window using three different specification limits of remaining Cu plating thickness for comparison sake. Also illustrated on the graph is the total time required to 1X (50 seconds) and 2X (100 seconds) rework the DIMM connector assembled on the same test vehicle. Based on this, it can be seen that both Alloy C and D are capable of performing up to a 2X rework using any of the three specification limits listed. Alloy B is capable of performing a 1X rework using any of the three specification limits, however falls short of being able to complete a 2X rework. Finally, Alloy A along with SAC305 and 405 are capable of performing a 1X rework, however, only when using a specification limit of 0.2mils of remaining Cu or less. All three are incapable of completing a 2X PTH rework.



**Figure 16.** Relative Cost of Alloy Compared to Sn-Pb

### Process Considerations

- Having multiple Pb-free alloys used within the manufacturing process will require strict material segregation and monitoring to reduce the chance of contamination.
- Until effects of various contamination levels are completely understood, frequent monitoring of solder pot contamination levels would be required when altering the solder fountain alloy only.

### CONCLUSIONS

The high Cu dissolution rates of SAC305/405 alloys are indeed the main driving factor in the requirement to change the Pb-free alloy used within the solder fountain rework process. This change could also potentially drive a change in the alloy used within the wave solder attach process in order to simplify the manufacturing process and reduce the degree of pot contamination during PTH rework. However, the push to replace SAC305/405 alloy with an alternative Pb-free alloy within the wave soldering process could easily be justified from a financial perspective in addition to technical justifications. Some of the alternative Pb-free alloys offer a 50% reduction in cost compared to SAC305/405 alloys, which can be quite significant if this saving is shared amongst multiple wave soldering machines.

This study indicated that there are three “alternative Pb-free alloys” (B, C and D) which could be used as potential replacements for the SAC305/405 alloy based on their Cu dissolution rate results. Each of the three alloys showed statistically similar dissolution rates to that of the Sn-Pb alloy. There are however, other considerations aside from Cu dissolution rates which need to be considered before selecting an appropriate alternative alloy. These include, the final joint quality produced as well as the reliability. In addition, supply chain considerations, logistics and costs are important factors in selecting a replacement Pb-free alloy.

### FUTURE WORK

Future work will include performing forced PTH reworks (1X and 2X) and reliability studies including ATC and mechanical testing to further understand the impact of Cu dissolution on PCB reliability. This will include both pure and mixed Pb-free conditions using the top three alternative

Pb-free alloys from this study. There is a large amount of data available on solder joint reliability using SAC305/405 alloy, but further testing will be required if an alternative Pb-free alloy is chosen for PTH processes, especially primary attach. Provide recommendations to include specific IPC specifications relating to remaining Cu plating due to Cu dissolution post PTH rework. In addition, steps required to implement an alternative Pb-free alloy into the manufacturing process will be taken such as performing initial validation by applying the development findings to controlled volume manufacturing conditions.

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