

Acceptance Testing Of Low-Ag Reflow Solder Alloys

Kris Troxel¹, Aileen Allen², Elizabeth Elias Benedetto³, Rahul Joshi³
Hewlett-Packard Company

¹Boise, ID, USA

²Palo Alto, CA, USA

³Houston, TX, USA

Kris.Troxel@hp.com

Abstract

Since the implementation of the European Union RoHS directive in 2006, the electronics industry has seen an expansion of available low-silver lead (Pb)-free¹ alloys for wave soldering, miniwave rework, BGA and CSP solder balls, and, more recently, solder pastes for mass reflow. The risks associated with the higher processing temperatures of these low-silver (Ag between 0-3 wt%) solder alloys, such as potential laminate or component damage, increased copper dissolution, and reduced thermal process windows may present manufacturing challenges and possible field reliability risks for original equipment manufacturers (OEMs). In order to take advantage of potential cost reduction opportunities afforded by these new alloys, while mitigating manufacturing and reliability risks, the company has defined test protocols [1-4] that can be used for assessing new Sn-Ag-Cu(SAC), Sn-Ag, and Sn-Cu alloys for general use in electronics.

This paper describes initial test results for low-silver alloys using these solder paste alloy assessment protocols for BGAs and leaded components, and the impact of the alloys on printed circuit assembly process windows. Specific pass/fail criteria for acceptance of an alloy are not included, however, as they may vary across industry segments. The assessment evaluates wetting behavior, solder joint thermal fatigue and mechanical shock reliability, intermetallic formation, general physical joint acceptability, and copper dissolution. The variables include multiple component types: two BGA components with the same paste/ball alloy combinations, and numerous leaded components that include common component platings.

Surface mount (SMT) process temperature windows are typically constrained on the low end by the ability to melt solder and form acceptable joints, and on the high end by the maximum process temperatures of other materials, such as components. These two constraints have led to a process window of approximately 25°C when soldering with more conventional, Sn-3.0Ag-0.5Cu paste. Low-silver SMT alloys have been found to reduce the thermal process window even further.

Background

During the industry transition from Sn-Pb to Pb-free solder in the early 2000s, significant work was performed by the iNEMI consortium to develop assembly process limits to both produce acceptable solder joints as well as protect other materials from damage. This work was originally presented at ECTC 2005 [5]. This presentation defined the characteristics of the acceptable process window for process alloys in the range of SAC305-SAC405 (Sn 3.0-4.0Ag 0.5Cu). It mandates that each and every solder joint has to reach at least 230°C during reflow to produce acceptable and reliable joints. In addition, this previous work [6] defined the minimum peak temperature for SAC305 as 230-232°C, but theorized that low-Ag alloys may only increase that temperature by 5-7 degrees Celsius.

Solder alloys used in Surface Mount Technology (SMT) will generally require lower liquidus temperatures than those alloys used in wave soldering. SMT process temperature windows are typically constrained on the low end by the ability of the solder to melt and form good joints, and on the high end by the maximum exposure temperatures of the other materials, such as components or laminates. These two constraints have led to a process window of approximately 25°C with more conventional, Sn-3.0Ag-0.5Cu paste. Low-silver SMT alloys have been found to reduce the thermal process window even further. While the liquidus temperature is the theoretical minimum peak temperature that any solder joint must reach to start the wetting process, it is well known that this temperature is not always sufficient to produce acceptable joints on the various component plating surfaces. In addition, non-eutectic alloys remain pasty for several degrees and will often not produce acceptable joints until fully molten. It is therefore important to determine a minimum peak temperature at which a specific low-Ag alloy will repeatedly produce acceptable joints across the range of likely component sizes, platings, and PCB surface finishes. This minimum peak, or superheat, temperature is often 10-15°C higher than the liquidus point of the alloy. Superheat is defined as the temperature necessary to dissolve native oxides of metals, which is higher than the liquidus temperature. For low-silver reflow alloys with liquidus temperatures of 225-228°C, this produces a theoretical minimum peak of 240°C or higher. Extending the time above liquidus is sometimes used to improve solder joint formation but can cause increased intermetallic formation.

¹ Pb-free does not technically mean no Pb, as it allows Pb in concentrations up to 1000 ppm. When the phrase Pb-free is used in this paper, this is meant to indicate that the material is RoHS-compliant.

Maximum component temperatures, which define the upper limit of a process window, are often defined by the supplier, but in-lieu of clear limits the J-STD-020[7] classification requirements, based on package size, are typically used. Table 4-2 of the J-STD-020 will define the maximum peak component temperature for any given package on a PCA (Printed Circuit Assembly), with typical PCAs containing a range of components. The range of maximum package temperatures is between 245°C and 260°C. Many PCA designs contain a wide range of component sizes creating complexity in reflow oven program generation. It is typical to use the largest component to set the maximum peak temperature for a reflow profile, as it will typically be the coolest part of the board. Using Table 4-2 to define the maximum temperature for a large package will create a minimum peak temperature as high as 245°C.

An additional complication is the need to reach this minimum peak temperature at every solder joint across the entire PCA. Even with sophisticated reflow ovens, it is often difficult to keep the temperature delta across a complex or thermally massive PCA within 15°C.

The data presented here (see Table 1) is based on four low-Ag alloys' data submitted by multiple alloy vendors over two years. These alloys are commercially available, and have different dopant concentrations. The next section details the test methods for alloy evaluation. The subsequent section details the test results.

Table 1: Liquidus temperatures of the alloys reviewed in this paper

Alloys Evaluated	Ag content	Liquidus Temperature (°C)
A	0.3%	226
B	0.3%	228
C	0.3%	227
D	1.0%	225

Test Methods

The test protocol described below reflects the company's standard evaluation procedure for reflow alloys for general electronics assembly use. For all of the tests the following were specified: industry standards and test boards where available, appropriate controls (an alloy currently used widely in production), test parameters and execution details. The tests address both reliability and manufacturability concerns when soldering with a low-Ag alloy.

Manufacturing DoEs

There were two manufacturing design of experiments (DoEs) as part of each SMT alloy evaluation. Both consisted of building boards with a low-Ag SMT alloy and a SAC305 control at defined process parameters (with multiple peak reflow temperatures and times above liquidus, TAL). Small test boards were selected for each DoE so that they could be processed with very small temperature deltas across the boards, eliminating this variable. This gave confidence in the DoE results on whether an alloy was able to form acceptable solder joints at each specified temperature and TAL.

BGA solder joints were evaluated for two different sizes of BGA component (see test board in Figure 1). In this DoE, three parameters were evaluated: BGA solder joint formation (in cross-section) per IPC-A-610 [8], intermetallic compound (IMC) thickness, and Cu dissolution.

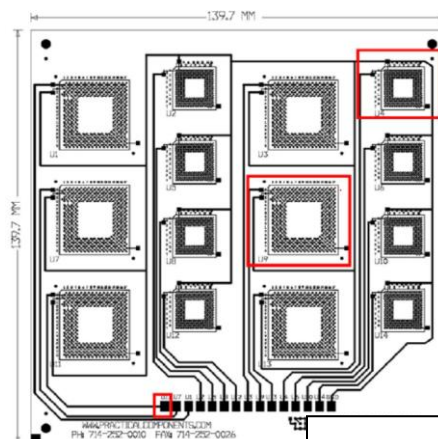


Figure 1: BGA Manufacturing DoE Test Board. Boxed locations (U4, U9, PCB pad for U11) are thermocouple locations.

The second DoE evaluated numerous leaded components (see test board in Figure 2). In this DoE, leaded solder joint

formation per IPC-A-610 was assessed for the low-Ag alloy.

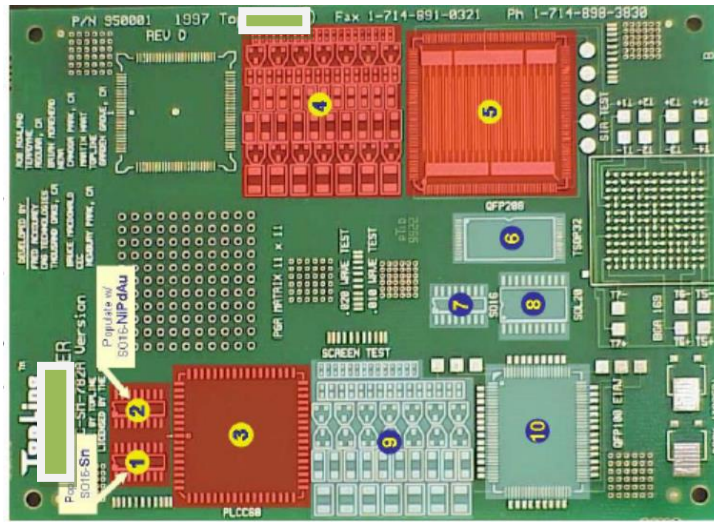


Figure 2: Leaded component DoE test board. Numbered components are to be populated (1-5 to be cross-sectioned). Ref: SMTA Saber

For the low-Ag alloy to be feasible for use in general PCA assembly, it must not dissolve excessive amounts of Cu, it must not form very thick IMCs that might be prone to fracture under mechanical stresses, and it must form acceptable solder joints within the OEM’s PCA processing window. The first two requirements (Cu dissolution, IMC thickness) were evaluated at a single process condition, 250 °C and 120 seconds TAL, processed three times. This process condition was selected as representative of the PCA process conditions of a complex product board that is reworked twice. This would be the worst-case conditions, from an IMC growth and Cu dissolution standpoint. The last requirement, forming acceptable solder joints, was the basis for the wide range of TALs and peak reflow temperatures in both DoEs; ranges beyond what would be considered a normal process window, but necessary to determine the processing cliffs where the low-Ag alloy fails to form acceptable solder joints. An example of the manufacturing DoE process conditions is in Table 2.

Table 2: Example process conditions for manufacturing DoE.

		Time Above Liquidus*			
		15 sec	30 sec	60 sec	120 sec
Peak Reflow Temperature	230 °C	Green	Yellow	Green	Yellow
	240 °C	Yellow	Green	Yellow	Green
	250 °C	Yellow	Green	Yellow	Green
	265 °C	Do not build	Yellow	Green	Yellow

*Note that the liquidus temperature varies by alloy composition.

Of the 15 process conditions assembled, a subset (green boxes) was selected for cross-sectioning and inspection to determine BGA solder joint formation per IPC-A-610, IMC thickness, and Cu dissolution. If questions arose on the data, additional process conditions (yellow boxes) may be evaluated.

Wetting balance was evaluated for the low-Ag alloys (compared to SAC305) by following industry test method J-STD-003[9]. A sample size of 10 coupons, per alloy, was used. A standard activated rosin flux #2 for Pb-free alloys was specified to keep different vendor test results consistent. The test boards were preconditioned for 8 hours at 72 °C/85% RH, followed by 1 hour at 105 °C. For the wetting balance test, the coupons were immersed in molten solder, 45° incident to the solder pot, to a depth of 0.4 mm at 2 mm/second.

Reliability Tests

The reliability tests included accelerated thermal cycling (ATC) and mechanical shock testing. Both these tests used BGAs processed at a single process condition that formed acceptable solder joints (per IPC-A-610). The BGA Manufacturing DoE Test Board (see Figure 1) was used for both reliability tests, populated with the eight smaller CABGA-192 components.

Mechanical shock testing was performed per JEDEC standard JESD22-B111[11] (test condition B, 1500 G, 0.5 ms duration, half-sine pulse). The controls were Sn-37Pb and SAC405. For all alloys tested, the solder ball and SMT paste were the same alloy (no mixing of solder compositions was chosen, since a low-Ag alloy ball with SAC305 paste should have intermediate performance between a low-Ag alloy and a SAC305 solder joint). For each alloy, the mechanical shock performance was evaluated on Cu OSP and electrolytic Ni/Au PCB surface finishes. Resistance was monitored in-situ, Weibull failure plots generated, and failure modes verified with selective failure analysis after test completion.

ATC testing was executed per IPC-9701[10] (test condition 1) to 6000 thermal cycles. The controls were Sn-37Pb and SAC305. The test board had a Cu OSP surface finish. For all alloys tested, the solder ball and SMT paste were the same alloy, for the same reasons discussed above for mechanical shock testing. Resistance was monitored in-situ, Weibull failure plots generated, and failure modes verified with selective failure analysis after test completion.

Bulk Solder Material Properties

Bulk solder material properties evaluated included melting behavior (DSC or DTA curves per NIST SP 960-15[12]), stress-strain curves (with a specified sample geometry per ASTM E8-04[13]), elastic modulus (per ASTM 1875-00[14]), coefficient of thermal expansion (per ASTM E831-06[15]), density, hardness (per ASTM E92-82[16]), electrical conductivity (per ASTM B193-02[17]), and thermal conductivity.

Test Results and Discussion

Manufacturing DoE Results

IMC Thickness

Measured on BGA Manufacturing DoE Test Boards (see Figure 1) that were reflowed 3 times with a peak reflow temperature of 250 °C and 120 seconds TAL.

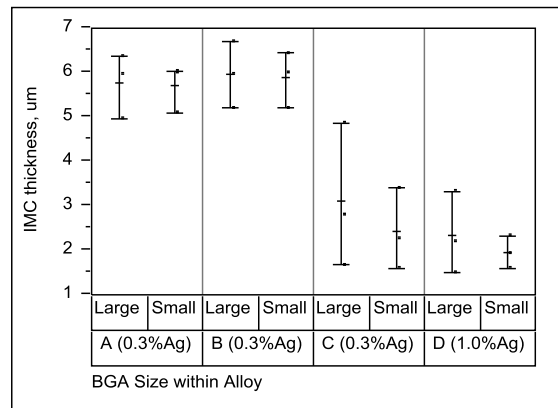


Figure 3: IMC thickness distribution by Alloy (A-D) and BGA size (large/small)

Table 3: Summary of IMC thicknesses (microns)

Alloy	BGA	Count	Mean	Std Dev	Min	Max
A (0.3%Ag)	Large	216	6.0	0.3	5.0	6.4
	Small	216	6.0	0.3	5.1	6.0
B (0.3%Ag)	Large	216	6.0	0.3	5.2	6.7
	Small	216	6.0	0.3	5.2	6.5
C (0.3%Ag)	Large	216	2.8	0.8	1.7	4.9
	Small	216	2.3	0.4	1.6	3.4
D (1.0%Ag)	Large	216	2.2	0.4	1.5	3.3
	Small	216	1.9	0.2	1.6	2.3

Two BGA body sizes were evaluated [14 mm and 23 mm]. IMC thicknesses for alloys A and B were normally distributed with no significant difference between the large and small BGA. For alloys C and D, greater variability in the large BGA IMC thickness resulted in values significantly different than smaller BGA (as seen in Figure 3 and Table 3).

Copper Dissolution

This was measured on the BGA Manufacturing DoE Test Boards (see Figure 1) that were reflowed 3 times with a peak reflow temperature of 250°C and 120 seconds TAL.

Cu thickness measurements were made at each solder joint, in the middle of the joint and underneath the soldermask adjacent to the joint. Cu removed was the difference in copper thickness at these two locations. Cu dissolved was determined by subtracting Epsilon (thickness of Cu removed during soldermask etch in the PCB fab process) from the Cu removed values.

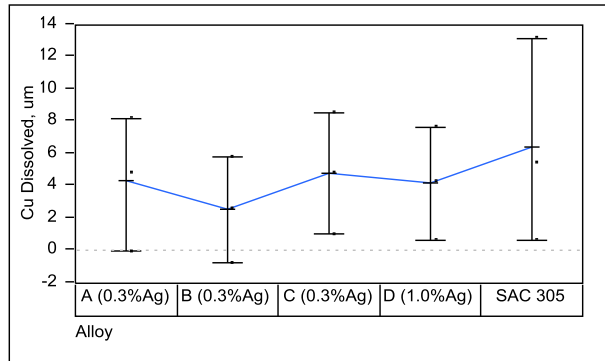


Figure 4: Cu dissolution distribution by alloy

Table 4: Summary of Cu dissolved (microns)

Alloy	BGA	Count	Mean	Std Dev	Min	Max
A (0.3% Ag)	Large	48	4.6	2.1	0.3	8.2
	Small	48	5.2	1.7	1.0	7.7
B (0.3% Ag)	Large	48	2.6	1.6	0	5.3
	Small	48	2.7	1.4	0.4	5.8
C (0.3% Ag)	Large	48	5.4	1.2	2.9	8.6
	Small	48	4.3	1.5	1.1	7.3
D (1.0% Ag)	Large	48	5.2	1.6	1.3	7.7
	Small	48	3.5	1.5	0.7	6.7
SAC305	Large	48	6.1	2.1	2.5	13.2
	Small	48	5.0	2.3	0.7	9.5

The amount of Cu dissolved after soldering was less for the low silver alloys than that for SAC305. The Cu dissolution results were normally distributed for the evaluated alloys but varied with alloy and BGA size (as seen in Figure 4 and Table 4). The Cu dissolution performance varied by BGA size, though not in a consistent fashion. While alloy B showed comparable Cu dissolved values between the 2 BGA sizes, alloy C and D both had more Cu dissolved for the larger BGA while alloy A had greater Cu dissolution values for the small BGA (this could be attributable to bare board Cu characteristics between the different vendors).

Acceptability of Solder Joints

Solder joints of the leaded DoE test board (SMTA Saber) assemblies using the respective low-Ag paste alloys were evaluated to the IPC-A-610E criteria. A range of lead and joint types such as J-leads, gull-wing leads and passive components were inspected. However, BGA joints were not inspected due to lack of access for visual inspection.

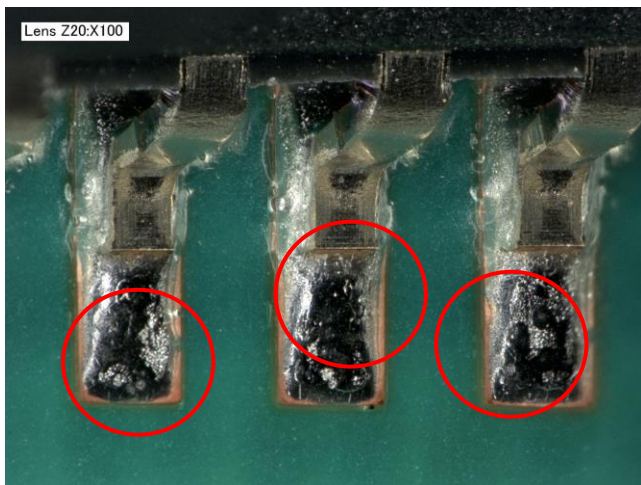
Solder defects such as cold solder and lack of fully reflowed paste were found across all low-Ag alloys and all process conditions of 230°C and 240°C. Cold solder is defined per IPC-A-610 as “a solder connection that exhibits poor wetting, and that is characterized by a grayish, porous appearance. (This is due to excessive impurities in the solder, inadequate cleaning prior to soldering, and/or the insufficient application of heat during the soldering process.) Defects (see Figures 5-

10) appeared randomly distributed across the PCAs. Acceptable solder joints were observed on boards processed at 250°C and times above liquidus of at least 60 seconds (see Table 5).

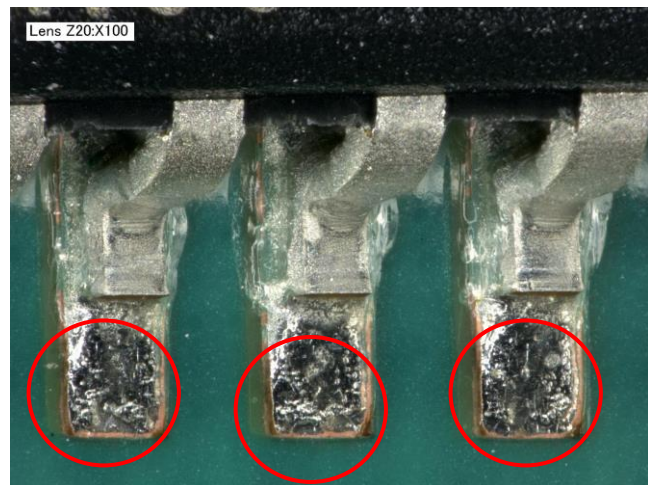
Table 5: Visual inspection summary of soldering acceptability criteria per IPC-A-610E

	PCA process peak reflow temperature		
Alloy	230°C	240°C	250°C
A (0.3% Ag)	Multiple instances of defects such as unreflowed/ uncoalesced and cold solder joints	Multiple instances of defects such as unreflowed/ uncoalesced and cold solder joints	Generally acceptable solder joints
B (0.3% Ag)			Multiple instances of defects such as unreflowed/uncoalesced and cold solder joints
C (0.3% Ag)		Marginally acceptable joints with random defects of cold solder	Generally acceptable solder joints
D (1.0% Ag)			

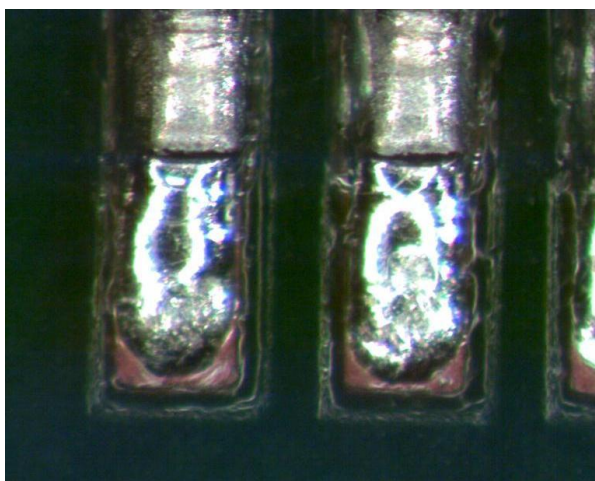
Examples of the observed defects:



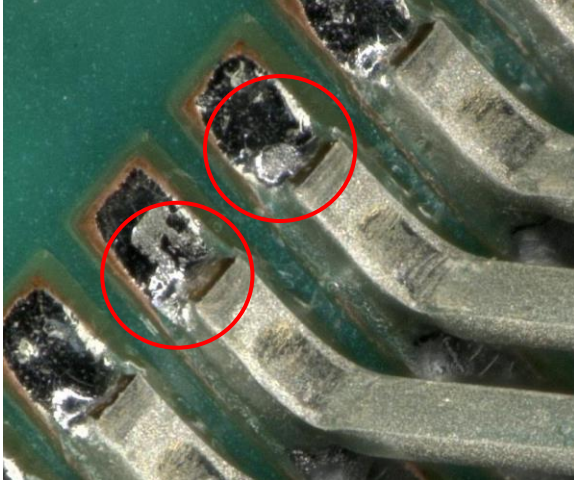
**Figure 5: Low-Ag Alloy A - Peak 240°C at 60 sec TAL
Uncoalesced/Unreflowed solder paste**



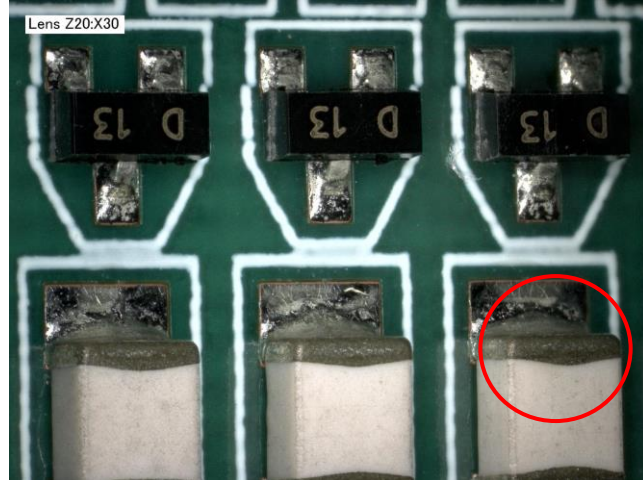
**Figure 6: Alloy A - Peak of 230°C at 120 sec TAL
Uncoalesced/Unreflowed solder paste**



**Figure 7: Alloy A – Peak of 240°C at 60 sec TAL
Uncoalesced/Unreflowed solder paste**



**Figure 8: Alloy A – Peak of 240°C at 60 sec TAL
Cold Solder**



**Figure 9: Alloy B – Peak of 240°C at 60 TAL
Cold Solder**

**Figure 10: Alloy B – Peak of 240°C at 30 sec TAL
Cold Solder**

X-ray evaluation of low-Ag SMT solder joints also showed several instances of unusually high levels of voiding as shown in figure 11. While voiding at this level is not considered a defect, it was found to be generally higher than seen in typical SAC305 SMT joints.

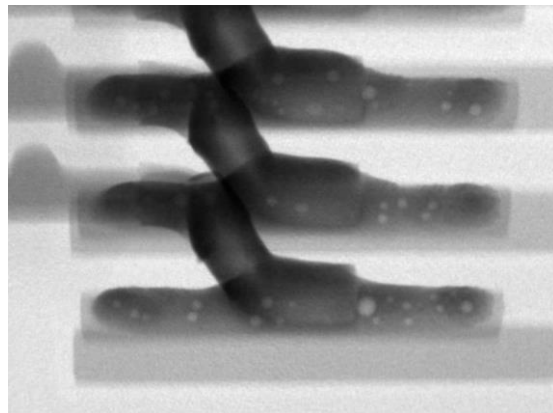


Figure 11: Example of voiding observed

Mechanical Shock:

Alloy A (0.3% Ag) had comparable drop/shock performance to Sn-37Pb and better performance than SAC405 in both electrolytic Ni/Au and Cu OSP surface finished boards. The solder joint failure mode during mechanical shock testing was predominately cracking in the intermetallic layer/bulk solder near the PCB side for both Alloy A and SAC405, while Sn-37Pb solder joints failed on both the component and PCB side in the bulk of the solder, as well as at the PCB IMC layer.

Alloy B (0.3% Ag) had similar drop/shock performance to Sn-37Pb and SAC405 on both electrolytic Ni/Au and Cu OSP boards. The solder joint failure mode during mechanical shock testing varied by alloy but not by surface finish. Alloy B (0.3% Ag) solder joint failures were in the solder near the PCB intermetallic compound (IMC) layer.

The drop/shock performance of alloys C (0.3% Ag) and D (1.0% Ag) were similar for both electrolytic Ni/Au and Cu OSP boards. They both performed worse than Sn-37Pb but better than SAC405. The solder joint failure modes for alloys C and D were also similar - predominately cracking in the intermetallic layer on the PCB side.

Table 6: Relative mechanical shock performance of Alloys A-D compared to their controls, on Cu OSP and Electrolytic Ni/Au board finishes

Mech Shock	Board Finish	Drops to Failure (β , η)	Performance relative to:	
			SAC405	Sn-37Pb
A (0.3%Ag)	Electrolytic Ni/Au	3.1, 29.0	2.2X	1.1X
	Cu OSP	3.4, 36.2	1.7X	1.2X
B (0.3%Ag)	Electrolytic Ni/Au	1.2, 133.0	1.3X	4.2X
	Cu OSP	1.0, 146.0	1.6X	0.8X
C (0.3%Ag)	Electrolytic Ni/Au	2.3, 5.2	2.8X	0.2X
	Cu OSP	3.6, 11.7	3.8X	0.3X
D (1.0%Ag)	Electrolytic Ni/Au	2.6, 6.8	3.7X	0.2X
	Cu OSP	2.9, 10.6	3.5X	0.3X

Note 1: β and η are the shape and scale parameter of a 2-parameter Weibull distribution

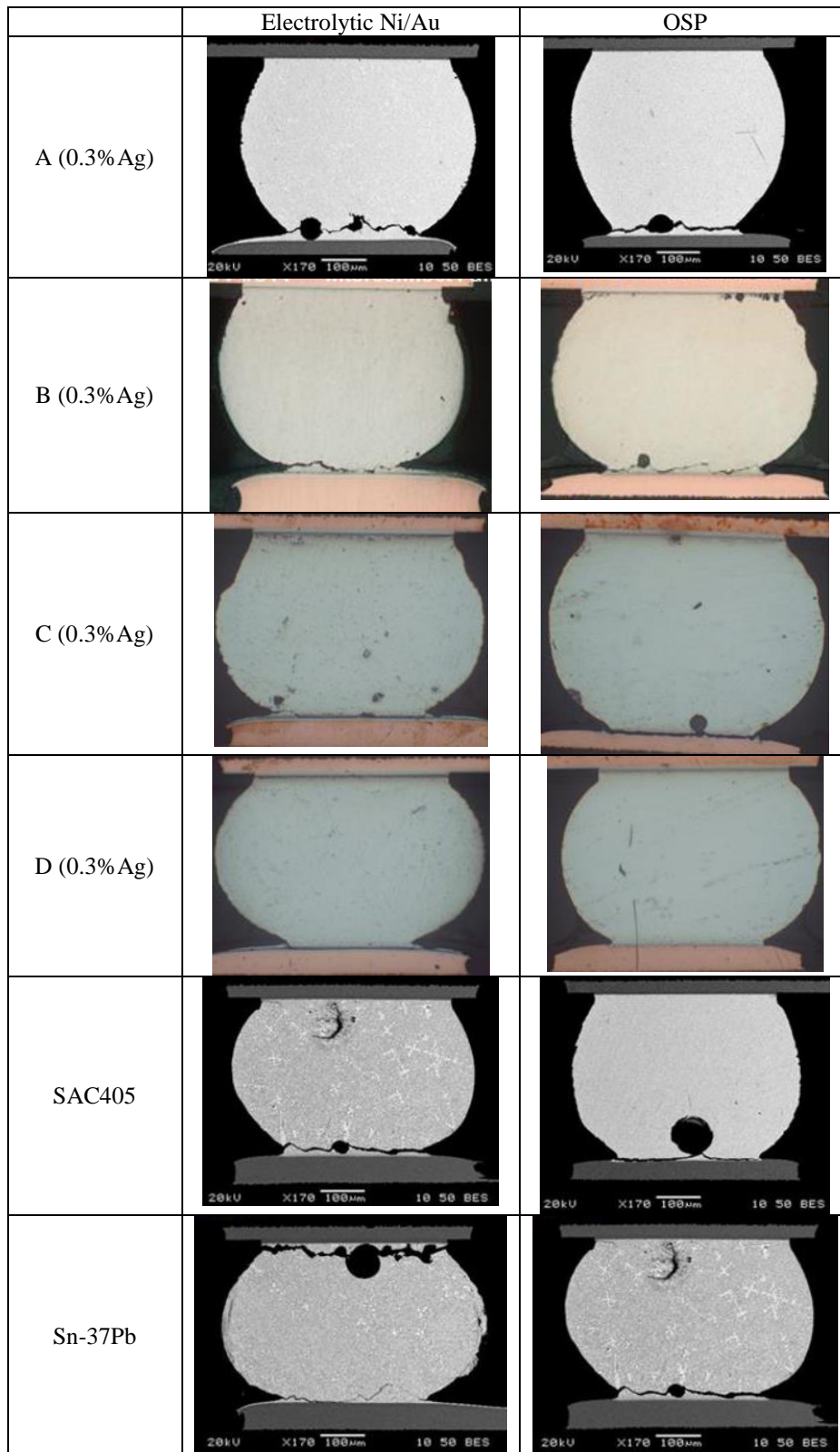


Figure 12: Post Mechanical Shock solder joint cross-sections for paste alloys

Accelerated Temperature Cycling:

In accelerated thermal cycling (0-100 °C, 10 minute ramps and dwells, to 6000 cycles), all four low-Ag alloys performed better than Sn-37Pb. Alloy A (0.3% Ag) and alloy D (1.0% Ag) did not have any electrical failures nor was any damage seen in cross-sections after 6000 ATC cycles. Alloy B (0.3% Ag) had 100% failures by 4857 ATC cycles and its performance was still better than Sn-37Pb. Alloy C (0.3% Ag) only had 4 parts out of 32 fail at 6000 thermal cycles, when the test was terminated.

The solder joint failure mode in accelerated thermal cycling was in the bulk solder near the component interface for the alloy B (full opens), alloy C (full opens), SAC305 (partial opens) and Sn-37Pb (full opens).

Table 7: Relative accelerated thermal cycle performance of Alloys A-D compared to their controls

ATC	Result	Performance relative to:	
		SAC305	Sn-37Pb
A (0.3% Ag)	No failures up to 6000cyc	Same	> 1.4X
B (0.3% Ag)	32/32 failures by 4857cyc	< 0.9X	1.5X
C (0.3% Ag)	4/32 failed by 5310cyc	< 0.8X	> 1.2X
D (1.0% Ag)	No failures up to 6000cyc	Same	> 1.4X

Note 1: Alloy B and Sn-37Pb had 100% failures,

Note 2: '>', '<' signs used to indicate alloy performance relative to the controls based on # failures

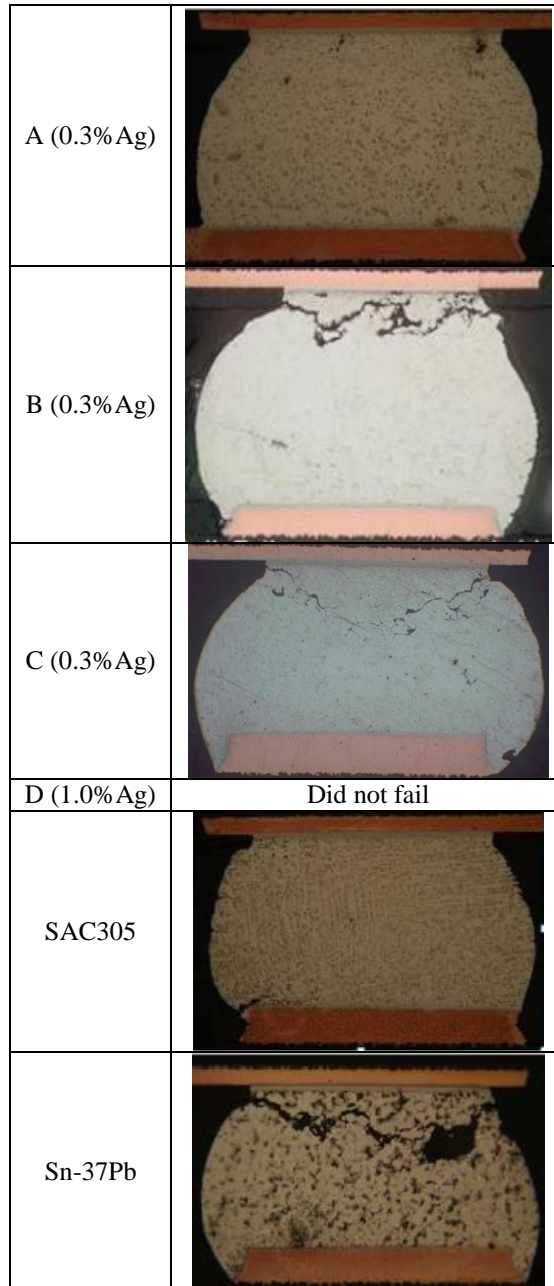


Figure 13: Post ATC solder joint cross-sections for paste alloys

Conclusions

Prior studies of low-Ag alloys primarily investigated BGA ball alloys and had not fully explored the implications of increased liquidus temperature on reflow paste alloys. This work found the peak reflow temperature has to be increased by 10-15 °C over the liquidus temperature when using low-Ag paste alloys.

For the alloys studied, this implies that a minimum reflow peak temperature of 240°C is required. When combined with the maximum package temperature of 245°C, this results in an effective process window of 0-5°C, when accounting for temperature deltas across the board. However, if solder joints are properly formed, reliability (thermal fatigue, mechanical shock) of low-Ag alloys is comparable to SAC305. The drivers for whether a low-Ag reflow alloy is acceptable are board complexity and thermal mass. The challenge for assemblers is in developing reflow programs that minimize the temperature delta between the coolest and hottest locations on the board. Indeed, it is unlikely that an acceptable process window is feasible for general-use company PCAs using low-Ag SMT alloys ($\leq 1\% \text{Ag}$). Low-Ag alloys with liquidus temperatures closer to SAC305 ($< 220^\circ\text{C}$), and those with near-eutectic melting characteristics, appear more suitable candidates for general use; however, this will require either an increase in Ag content or in dopant selection.

References

- [1] Elizabeth Benedetto et al, "Acceptance Testing of Pb-free Bar Solder Alloys," SMTAI 2013.
- [2] Helen Holder et al, "Test Data Requirements for Assessment of Alternative Pb-Free Solder Alloys," SMTAI 2008.
- [3] Aileen Allen et al, "Acceptance Testing of BGA Ball Alloys," ECTC 2010.
- [4] Gregory Henshall et al, "Progress in Developing Industry Standard Test Requirements for Pb-Free Solder Alloys," IPC Printed Circuits Expo®, APEX® and the Designers Summit 2010.
- [5] Pb-free Assembly, Rework and Reliability Analysis of IPC Class 2 Assemblies, Jerry Gleason, et al, ECTC, 2005.
- [6] iNEMI Pb-Free Alloy Alternatives Project Report: State of the Industry, Greg Henshall, et al, SMTAI, 2009.
- [7] IPC/JEDEC J-STD-020, Moisture/Reflow Sensitivity Classification for Nonhermetic Solid State Surface Mount Devices.
- [8] IPC-A-610E, Acceptability of Electronic Assemblies.
- [9] IPC J-STD-003, Solderability Tests for Printed Boards.
- [10] IPC-9701, Performance Test Methods and Qualification Requirements for Surface Mount Solder Attachments.
- [11] JEDEC JESD22-B111, Board Level Drop Test Method of Components for Handheld Electronic Components.
- [12] NIST Special Publication 960-15, NIST Recommended Practice Guide: DTA and Heat-Flux DSC Measurements of Alloy Melting and Freezing.
- [13] ASTM E8-04, Standard Test Methods for Tension Testing of Metallic Materials.
- [14] ASTM 1875-00, Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio by Sonic Resonance.
- [15] ASTM E831-06, Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis.
- [16] ASTM E92-82, Standard Test Method for Vickers Hardness of Metallic Materials.
- [17] ASTM B193-02, Standard Test Method for Resistivity of Electrical Conductor Materials.