

# **iNEMI Pb-FREE ALLOY ALTERNATIVES PROJECT REPORT: STATE OF THE INDUSTRY**

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## **ABSTRACT**

Recently, the industry has seen an increase in the number of Pb-free solder alloy choices beyond the common near-eutectic Sn-Ag-Cu (SAC) alloys. New wave solder alloys have been developed with the intent of addressing concerns with copper dissolution, barrel fill, wave solder defects, and the high cost of alloys containing significant amounts of silver. Concerns regarding the poor drop/shock performance of near-eutectic SAC alloys led to the development of low Ag alloys to improve the mechanical strength of BGA and CSP solder joints. Most recently, investigations into new solder paste alloys for mass reflow have begun. The full impact of these materials on printed circuit assembly (PCA) reliability has yet to be determined.

The increasing number of Pb-free alloys provides opportunities to address the important issues described above. At the same time, the increase in choice of alloys presents challenges in managing the supply chain and introduces a variety of risks, particularly to the reliability of PCAs.

This paper provides the results of an iNEMI study of the present state of industry knowledge on Sn-Ag-Cu alloy

“alternatives,” including an assessment of existing knowledge and critical gaps. Focus areas are recommended for closing these gaps, with the additional goal of avoiding repeated investigations into issues already resolved. Finally, efforts to update industry standards to account for the new alloys and to better manage supply chain complexity and risk are described.

Key words: Lead-free alloys, alternative alloys, low silver alloys, microalloying, reliability

## **INTRODUCTION**

Within the past 2-3 years, the industry has seen an increase in the number of Pb-free solder alloy choices beyond the near-eutectic Sn-Ag-Cu (SAC) alloys most companies chose in order to meet the EU RoHS deadline of 1 July 2006. New wave solder alloys were developed with the intent of addressing concerns with copper dissolution, barrel fill, wave solder defects, and the high cost of alloys containing significant amounts of silver. Soon thereafter, the handheld product segment, especially mobile phone producers, became aware of the poor mechanical shock performance of near-eutectic SAC alloys. This motivated the development of low Ag ball alloys to improve the mechanical strength of

BGA and CSP solder joints, especially under dynamic loading conditions. Most recently, investigations into new solder paste alloys for mass reflow have begun. The full impact of these materials on PCA reliability has yet to be determined.

The increasing number of Pb-free alloys available provides opportunities to address the issues described above. At the same time, these alloy choices present challenges in managing the supply chain and introduce a variety of risks. For example, high melting point, low Ag alloys represent a risk in the reflow process if not managed properly. They may also present risks for thermal fatigue failure of solder joints in some circumstances, though much appears to be unknown about the impacts of Ag, Cu, and dopant concentration on thermal fatigue resistance of these alloys. Further, many “high reliability” OEMs have not switched to Pb-free technology and have rigorous requirements for evaluation and qualification of Pb-free materials and processes. The introduction of new alloys creates a “moving target” for these companies in making their transition (or partial transition) to Pb-free technology. Also, experience with near-eutectic SAC alloys is small relative to Sn-Pb, but new alloys have even less of a database and track record. Overall, there is a general lack of knowledge throughout the supply chain regarding new Pb-free alloys, their properties, advantages, and risks.

Thus, the wide variety of Pb-free alloy choices is both an opportunity and a risk for the electronics industry. In order to take advantage of the former while minimizing the impact of the latter, much still needs to be learned and the visibility to existing knowledge needs to be improved. In addition, an assessment of critical knowledge gaps needs to be performed so that industry efforts can be focused on them and not on repeating investigations into issues already resolved. Further, standards need to be updated and improved to account for the new alloys and to better manage the risks they present.

Addressing these concerns is the goal of the recently formed iNEMI Alloy Alternatives Team. This team was formed as a result of a study done by the iNEMI High Reliability Task Force, which set out to identify remaining knowledge gaps for the Pb free transition. The Alloy Alternatives Team is comprised of representatives from 16 companies spanning the entire supply chain: solder suppliers, component suppliers, EMS providers, and OEMs.

It is recognized that OEMs and EMS suppliers need to manage the realities of increasing alloy choice; they cannot stop solder and component suppliers from innovating and bringing new alloys to market. Further, there are data showing that some of the new alloys look promising and may provide improvements over the long run. Alloy improvements are a natural part of Pb-free technology maturing. Perhaps it would be ideal if there was one alloy that met all needs, but this eventuality seems to be several years away at best. Thus, it is not the intention of the

iNEMI Alloy Alternatives project to select or promote any specific alloy. Rather, our focus is to promote investigation, extend knowledge, update standards, establish assessment methods to best manage the opportunities and risks created by alloy alternatives, and to establish guidelines for alloy selection.

Overall, the goals of this project are to: (1) help manage the supply chain complexity created by alloy choices, (2) address reliability concerns and, (3) highlight the opportunities created by the new Pb-free alloy alternatives. Specific goals in Phase 1 include:

- Assess existing knowledge and identify critical gaps related to new Pb-free alloys. Provide technical information to the industry that will make selection and management of alloys easier.
- Raise awareness of this information through publication and presentation of findings.
- Propose a methodology and set of test requirements for assessing new alloys.
- Work with industry standards bodies to address standards that require updating to account for new alloys.
- Use findings to drive follow-on work, if required, in Phase 2.

## CONSIDERATIONS IN ALLOY SELECTION

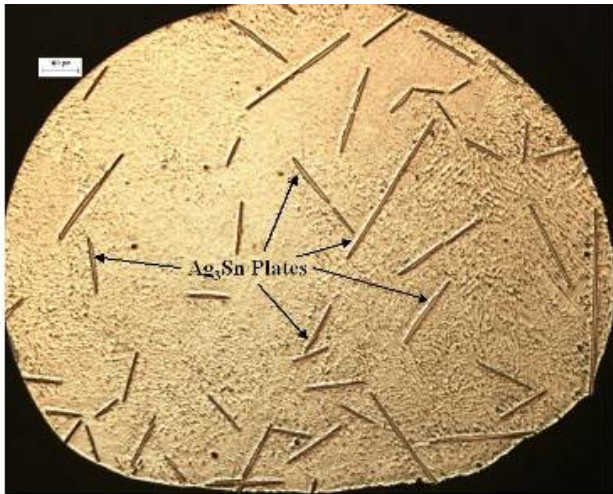
### The Evolution of Tin-Silver-Copper Alloys

The first phase of the transition to lead-free solder alloys was based around the Sn-Ag-Cu (SAC) eutectic. This was based initially on various industry consortia projects, such as the National Center for Manufacturing Center (NCMS) alloy down-selection study, and later strengthened by the original iNEMI Pb-free reliability study. There remains some uncertainty about the exact eutectic composition but the alloy commonly known as SAC405 (Sn-4.0Ag-0.5Cu) is thought to be close to the eutectic composition predicted by the thermodynamics. Although the initial motivation for the addition of silver to the tin-copper eutectic was the approximately 10°C reduction in melting point, the SAC alloys also exhibited a substantial increase in flow stress and improved thermal fatigue life. Because of concern about the cost of silver and in the hope of avoiding a patent held by Iowa State University, the Japanese Electronics Industry Association (JEITA) and then the IPC recommended use of the hypoeutectic alloy commonly known as SAC305 (Sn-3.0Ag-0.5Cu). However, many companies, particularly in Europe, chose to stay with the higher silver SAC405 because of the advantages that a eutectic alloy offers, in particular a lower incidence of shrinkage cavities and a lower melting temperature and pasty range.

The transition to Pb-free solder happened to coincide with a dramatic increase in the popularity of hand-held devices, such as cell phones, in which the disadvantage of the high flow stress of the high silver SAC alloys quickly became apparent. The high flow stress was accompanied by high stiffness, which led to brittle solder joint failures when these hand-held devices were accidentally dropped. These failures

occurred in the IMC layers between the bulk solder and the pad or by printed circuit board (PCB) “cratering.” The reason for these failures is that high stresses are transmitted to the IMC layers or to the underlying laminate rather than being absorbed by strain in the solder itself, as happened with the soft, highly compliant Sn-Pb eutectic solder. This topic is discussed in more detail later in the paper.

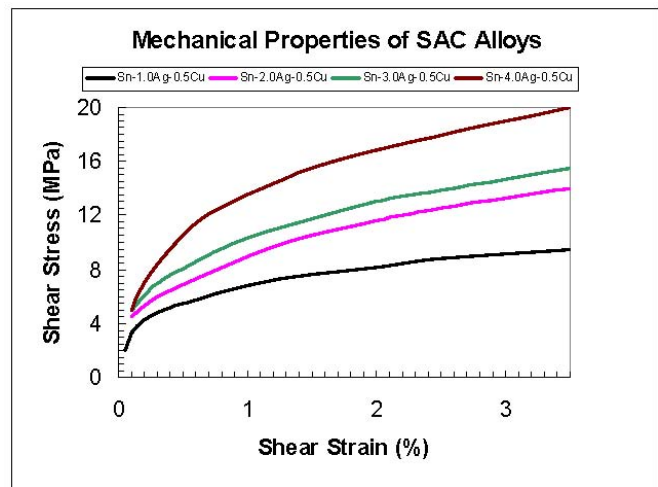
The high flow stress of the SAC alloys is at least partly the result of the network of platelets of the intermetallic compound (IMC)  $Ag_3Sn$  (Fig. 1). The volume fraction of these platelets is primarily a function of the silver content, so the first approach to improving performance in shock loading was to lower the silver content. This results in a more compliant alloy and a reduction in the flow stress (Fig. 2). The beneficial effect of the decreased strength and increased compliance on mechanical shock resistance is discussed later.



**Figure 1.** Cross section of an aged SAC405 solder sphere [29].

### Microalloy Fundamentals

Microalloying is the addition of an element other than the major constituents that has the effect of modifying the behavior of the alloy in a way advantageous to its performance. The level of the microalloying addition is typically 0.1% or lower. Thus, in parallel with the evolution of SAC alloys to lower levels of silver, the impact of microalloying additions to the properties of Sn-Cu eutectic has been explored. Such additions, such as Ni, have been shown to benefit the high strain-rate performance of Sn-Cu and SAC alloys. For example, Sweatman et al. [3] demonstrated improved fracture toughness at high strain rates through microalloy additions of Ni and Ge to eutectic Sn-Cu, Fig. 3.



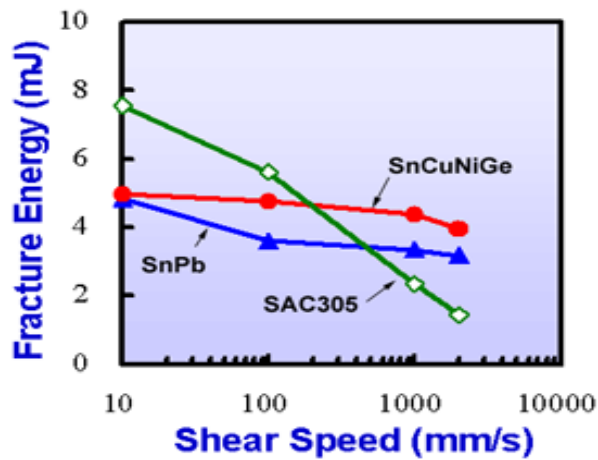
**Figure 2.** Mechanical (shear) properties of SAC alloys as a function of Ag content. Data from Ref. [1]

The performance issues with SAC305 have forced the industry to investigate (and offer) modified alloys with reduced or no silver, and with microalloy additions. Some problems and possible solutions are set out in Table 1.

**Table 1.** Problems with high silver SAC alloys and possible solutions.

| Problem               | Reduce or Remove Silver | Micro-alloy | Other Solutions                     |
|-----------------------|-------------------------|-------------|-------------------------------------|
| High Flow Stress      | X                       | X           |                                     |
| Brittle Joint Failure | X                       | X           |                                     |
| Low Impact Strength   | X                       | X           |                                     |
| Shrinkage Defects     | X                       | X           | Move Closer to Eutectic Composition |
| Copper Erosion        |                         | X           |                                     |
| Cost                  | X                       |             |                                     |

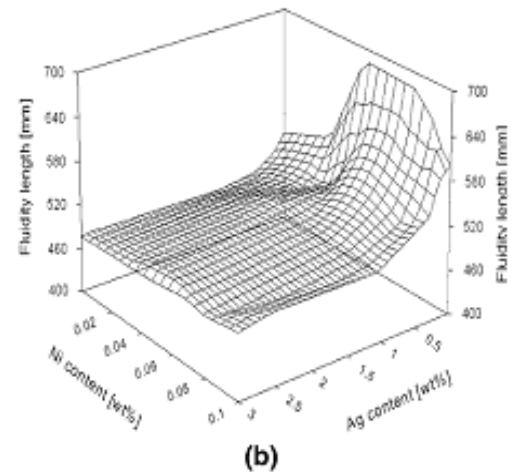
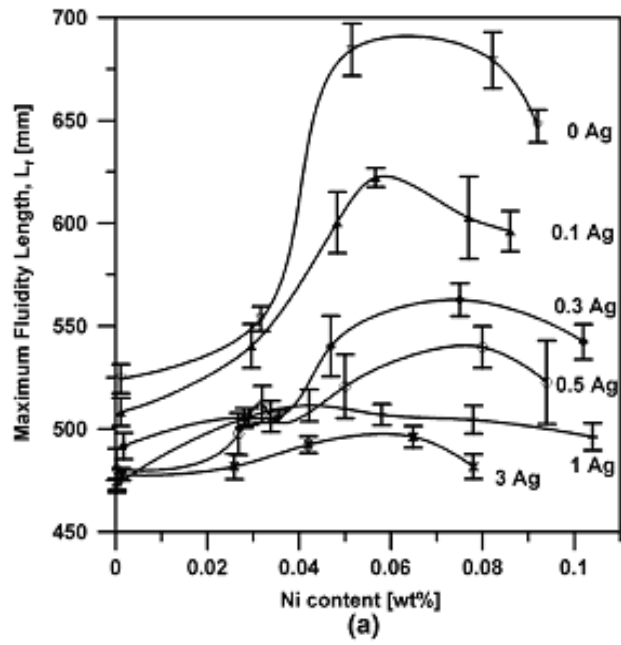
Some commonly investigated elements for microalloying are nickel (Ni), bismuth (Bi), phosphorus (P), germanium (Ge), cobalt (Co), indium (In), and chromium (Cr), with several already being used commercially. Some elements selectively incorporate into the interfacial intermetallic layer to: (1) control the IMC thickness, (2) slow the growth of the IMC in service, (3) modify its morphology, (4) prevent disruptive phase changes, and (5) increase toughness. Some microalloy additions go into solid solution within the tin matrix to increase both strength and ductility, and thus reliability, while others control oxidation. For example, the properties and behavior of the tin-copper-nickel alloy have been enhanced by additions of Ge and P as antioxidants [4].



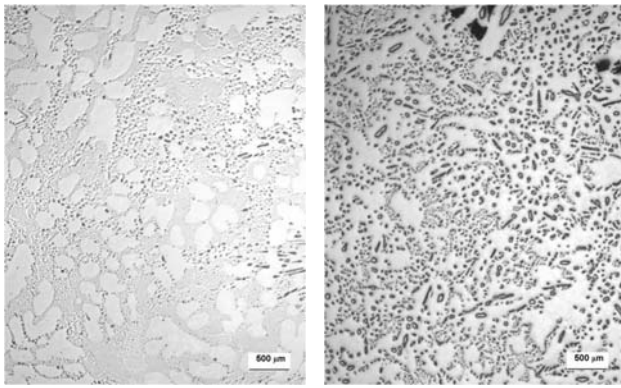
**Figure 3.** Fracture energy of 0.5mm BGA spheres as a function of shear impact speed [3].

Nickel is perhaps the most common microalloy additive. The beneficial effect of microalloying with nickel, which was first identified in the tin-copper eutectic, was found to extend to the low silver SAC alloy joints. For example the data in Fig. 4 show that Ni additions to SAC alloys can improve fluidity, which can be an advantage in wave soldering. As discussed later, Ni additions also improve the drop strength of low silver SAC alloys on copper pads, apparently due to the effect of nickel on the properties and behavior of the interfacial intermetallic layer. By incorporating into the intermetallic, the Ni facilitates nucleation of that phase so that the alloy can solidify directly as a eutectic without primary precipitation of tin dendrites (Fig. 5). Ni also inhibits diffusion, slowing the growth of the interfacial  $\text{Cu}_6\text{Sn}_5$  intermetallic (Fig. 6). The effect of an antioxidant, such as Ge, is to produce less dross and to provide resistance to tarnishing during exposure to elevated temperature.

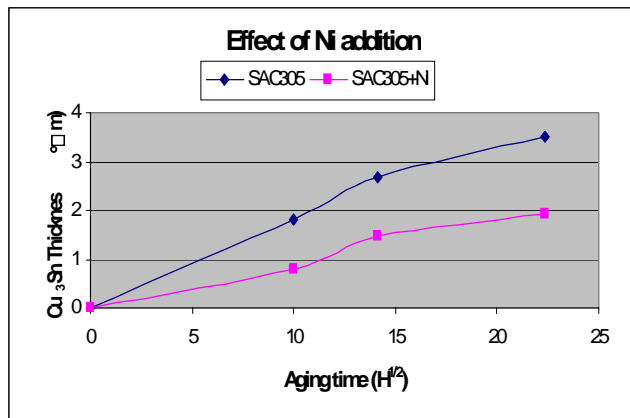
A limited number of other elements, including Co, added in concentrations less than 0.1% have also been found to have a beneficial effect on the tin-copper eutectic, similar to Ni. Bismuth improves wettability, contributes to interfacial IMC properties and bulk microstructure [4,5].



**Figure 4.** The maximum fluidity length of Sn-0.7Cu-yAg-xNi solder alloys at a constant superheat of  $T_{liq} + 40^\circ\text{C}$ . (a)  $L_f$  versus Ni content for six levels of Ag additions. Error bars indicate the standard deviation from six experiments. (b) A three-dimensional interpolation of the data shown in (a) Data from Ref [2].



**Figure 5.** Effect of nickel in preventing primary precipitation of Sn dendrites in Sn-Cu. Left: Sn-Cu. Right: Sn-Cu with Ni.



**Figure 6.** Effect of nickel on Cu<sub>3</sub>Sn intermetallic growth. Data from ref [3].

## THERMAL FATIGUE – SAC ALLOY ALTERNATIVES

### Development of Thermal Cycling Data

The combination of thermal fatigue and solder joint creep is considered a major source of failure of surface mount (SMT) components [6]. The standard technique for assessing susceptibility to low cycle fatigue failure commonly is referred to as thermal cycling or accelerated temperature cycling (ATC). The thermal fatigue reliability of eutectic Sn-Pb solder has received thorough treatment in the literature and generally is well understood. Reliability of Pb-free solders, however, continues to be a topic of intense study and debate as the conversion to Pb-free solder and processes proceeds throughout the electronics industry [7-11].

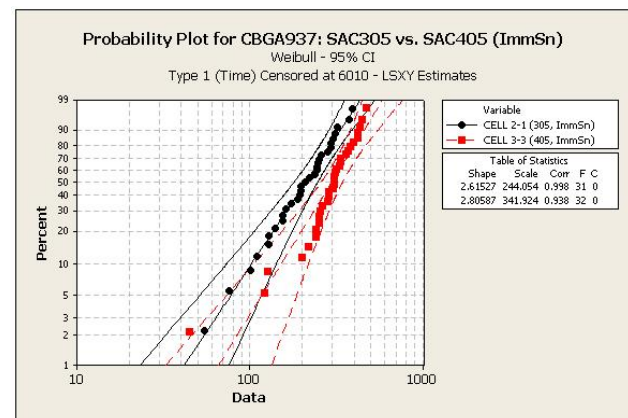
Due to resource limitations, the costs, and time required, only a few thermal fatigue studies have been performed on new Pb-free alloys. Although solder suppliers have played an active role in Pb-free solder development, there is little precedent for these companies to serve as a primary source for ATC fatigue data. OEMs and consortia, from which ATC data traditionally have originated, have yet to publish much ATC data on the new alloys.

## Challenges Evaluating ATC Test Data

Because ATC evaluations are driven by high reliability end use requirements, testing has focused on the high Ag content alloys, such as SAC405, 396, 387, and 305. Consequently, little thermal fatigue data exist for lower Ag alloys, such as SAC105. This poses a potential problem because the lower Ag alloys are being implemented in components used in products with long life, high reliability requirements. Further, there is no consensus on selection of test parameters, including dwell and ramp times, temperature extremes, and test duration. These factors hinder relevant comparisons, and as a result the literature contains contradictions and publications are not always complete.

## Thermal Fatigue of High Ag Content Alloys

There are minimal published data that directly compare thermal fatigue behavior of SAC405 to SAC305. Celestica compared both alloys within the same test program and their data, shown in Fig. 7, suggest that SAC405 may have better thermal fatigue reliability than SAC305 [12]. However, unpublished Unovis consortium data indicate that SAC 405 and 305 have comparable thermal fatigue reliability [13].



**Figure 7.** ATC test data showing better thermal fatigue performance for SAC405 compared to SAC305. The test vehicle was a 937 I/O CBGA [12].

## Thermal Fatigue of Low Ag Content Alloys

There is hardly any published data on thermal fatigue behavior of low Ag alloys, particularly in area array applications. Unpublished consortium test data on a custom area array substrate indicate that SAC405 and 305 have comparable thermal fatigue reliability but that SAC205 has slightly better reliability than either SAC405 or 305 [13]. One of the most detailed studies on a commercial area array component was by Kang et al. [14]. Their results suggest that a low Ag alloy will have better thermal fatigue reliability than a high Ag alloy.

A primary objective of the Kang study was to determine if low Ag content improved thermal fatigue resistance by minimizing formation and growth of Ag<sub>3</sub>Sn intermetallic platelets. Kang also examined cooling rate and thermal cycling profile using a CBGA package with a nominal

characteristic lifetime of 1000 cycles. The alloy comparison of interest in this study was SAC387 to SAC219.

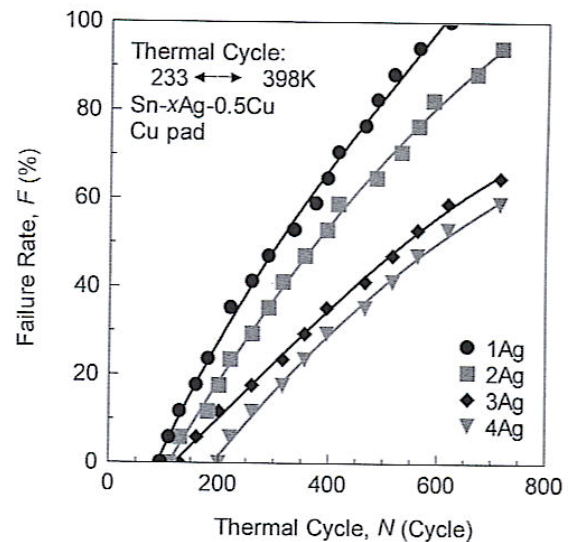
The ATC data from the Kang study are summarized in Table 2. The lowest lifetimes using the 0/100°C temperature cycle were recorded with the longest dwell time (120 min cycle). This confirms the hypothesis that SAC alloys have reduced reliability at longer dwell times. Slow cooling produced the best reliability regardless of ATC conditions, which the authors attributed to the improved microstructure. Slow cooling produces a coarser  $\beta$ -Sn microstructure that is more fatigue resistant, more ductile, and has lower residual stresses from SMT assembly. For the 120 min. cycle, the low Ag alloy (SAC219) recorded the best reliability. However, a systematic and consistent impact of Ag content on ATC life across all test conditions was not established, as indicated in Table 2.

**Table 2.** ATC test data from the Kang CBGA study [14].

| Alloy Composition<br>(cooling rate) | ATC Stress Conditions    |                           |                          |
|-------------------------------------|--------------------------|---------------------------|--------------------------|
|                                     | 0 to<br>100°C,<br>30 min | 0 to<br>100°C,<br>120 min | -40-<br>125°C,<br>42 min |
| Sn-3.8Ag-0.7Cu (Slow)               | 1,408<br>(7.25)*         | 1,012<br>(6.92)*          | 455<br>(6.12)*           |
| Sn-3.8Ag-0.7Cu (Fast)               | 1,164<br>(7.06)          | 982<br>(6.89)             | 392<br>(5.97)            |
| Sn-2.5Ag-0.9Cu (Slow)               | 1,212<br>(7.10)          | 1,108<br>(7.01)           | 446<br>(6.10)            |
| Sn-2.5Ag-0.9Cu (Fast)               | 1,200<br>(7.09)          | 1,054<br>(6.96)           | 384<br>(5.95)            |
| Sn-2.3Ag-0.5Cu-0.2Bi<br>(Slow)      | 1,212<br>(7.10)          | 953<br>(6.86)             | 407<br>(6.01)            |
| Sn-2.3Ag-0.5Cu-0.2Bi<br>(Fast)      | 1,130<br>(7.03)          | 934<br>(6.84)             | 376<br>(5.93)            |
| Sn-2.1Ag-0.9Cu (Slow)               | 1,224<br>(7.11)          | 1,188<br>(7.08)           | 372<br>(5.92)            |
| Sn-2.1Ag-0.9Cu (Fast)               | 1,064<br>(6.97)          | 1,012<br>(6.92)           | 384<br>(5.95)            |

Failure analysis showed that crack propagation was very near the package interface in the SAC387 alloy but was more into the bulk solder with the SAC219 alloy. It is possible that this finding indicates different failure modes for different Ag contents, but it apparently was not related to  $\text{Ag}_3\text{Sn}$  intermetallic platelets and was not discussed in detail by the authors.

In contrast to Kang's results, a study by Terashima et al. [15] found that increasing Ag content increases the thermal fatigue resistance of SAC solder. Their results, summarized in Fig. 8, show that: (1) the 1% Ag alloy had the fastest failure rate and (2) the 4% Ag alloy had twice the cycles to first failure ( $N_0$ ) as the 1% Ag alloy.



**Figure 8.** ATC test data from Terashima showing the direct relationship between Ag content and thermal fatigue life [15].

The Terashima work was limited to flip chip interconnects (not BGA balls) and the ATC cycle was -40/125 °C with approx. 15 minute dwells. Based on a detailed failure analysis, Terashima surmised that higher Ag content inhibited microstructural coarsening and prolonged fatigue life. The hypothesis that microstructural coarsening improves fatigue life is consistent with Kang. However, Terashima reported better reliability in the high Ag alloy, whereas Kang reported coarser structures and better reliability in the low Ag alloy in some cases. It is important to note that other authors have suggested that intermetallic particle coarsening also occurs during cycling and may play a role in fatigue life in conjunction with Sn dendrite coarsening [16].

To date, there are very limited published studies on the impact of microalloy additions on thermal fatigue performance. Recently, solder suppliers have begun generating such data. Pandher et al. recently published data that suggest the addition of bismuth (Bi) to low Ag alloys significantly improves temperature cycling performance, while other additives such as nickel have little to no effect in improving temperature cycling performance [5]. A full understanding of how microalloy additions affect thermal fatigue performance represents a major gap in our knowledge as an industry.

#### Survey of Ongoing Industry Thermal Fatigue Studies

Several industry ATC studies have been designed to address the thermal fatigue data gaps with low Ag and microalloyed solders. Those studies that are either planned or are underway include the following.

- **Industry Working Group (FLEX, HP, CSCO, SUN, XLNX, MOT)** – This group is testing Sn-3.5Ag, SAC105, and SAC305. The test vehicle is a Xilinx 676 PBGA used in a previous study [9]. ATC testing is nearing completion

using a 0 to 100 °C temperature cycle, with 10 minute ramps and dwells. Plans are to publish the results in due course.

- **Jabil Working Group (JBL, CKSNF, HP, AMKR, CSCO)** - This group is testing SACX (Sn-0.3Ag-7Cu+Bi), LF35 (Sn-1.2Ag-0.5Cu+Ni), SAC105, SAC205, SAC305, and Sn-37Pb. Four Amkor organic package types/sizes are being tested. The program has two phases: manufacturing impact and reliability, including thermal cycling. ATC testing will be performed with two thermal cycle profiles: 0/100°C and -40/125°C. The work is in progress [17,18] and the group expects to publish further results as they become available.

- **Alcatel-Lucent Working Group (ALU, LSI, CLS)** - This group is testing SAC405, SAC305, SAC105 and a Sn-Pb baseline. The package type is an LSI 680 PBGA which has been tested previously with SAC405 [10]. The program includes SMT and rework with thermal cycling at: 0/100°C with 10, 30, 60 minute dwells. The work is in progress and the group expects to publish results if all goes well.

- **Unovis** – Tests are in progress to evaluate multiple alloys using commercial and in-house test vehicles. Data initially will be limited to consortium membership.

- **HDPUG** – A multiple alloy (10 alloys) screening study is in progress. Thermal cycling will be performed at 0/100°C with 30 minute dwells. Data initially will be limited to consortium membership.

### Summary

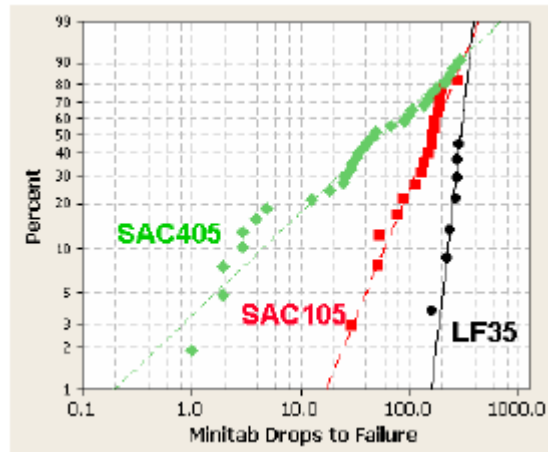
The following conclusions can be drawn from this brief review of thermal fatigue of SAC alternative alloys:

- Thermal cycling studies for low Ag content and microalloyed SAC solders are extremely limited.
- Some ATC results show better performance at low Ag contents, while others show better performance at high Ag contents. Thermal fatigue reliability appears to be dependent on process, microstructure, and microalloy content, and those dependencies have yet to be characterized fully and understood.
- Although significant quantities of data exist for high Ag alloys, the literature contains numerous contradictions, many due to differences in materials selection, processing, and alloy selection.
- A number of proprietary industry studies are either underway or in the advanced stages of planning. The results from these studies are expected to become public eventually.
- Prior to launching additional, independent thermal fatigue studies, researchers should review the literature and should also consider the scope, technical details, and timetables of existing experimental programs within the industry.

### MECHANICAL SHOCK RELIABILITY

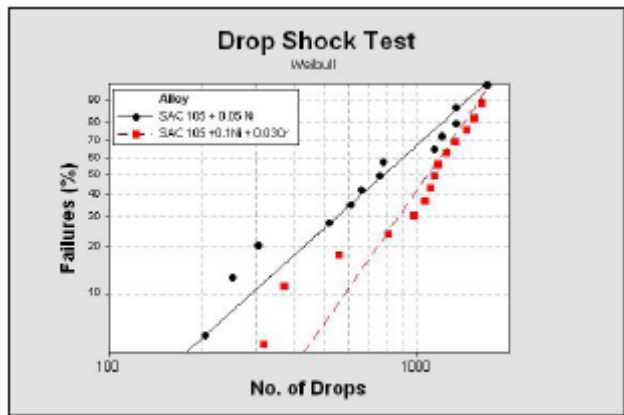
The major motivation for component and solder suppliers to develop new alloys for BGA/CSP solder balls was to improve the mechanical shock performance relative to SAC 305/405. In the past few years, a significant number of studies have been performed to assess the mechanical shock performance of new Pb-free alloy interconnections on area-

array packages. These studies consistently show that low Ag (<3%) SAC alloys perform better in mechanical shock (drop) testing than alloys with Ag content of 3% or more [4,19-22]. Fig. 9 illustrates this finding for two low Ag alloys relative to SAC405.



**Figure 9.** Mechanical shock performance for SAC405, SAC105, and LF35 (Sn-1.2Ag-0.5Cu+Ni). After Kim et al. [21].

Figure 9 also shows the positive impact that many studies have demonstrated on copper surfaces for the addition of microalloy additions, specifically the addition of Ni to the SAC125 base alloy for LF35. Another example is provided in Fig. 10 for the addition of 0.03% Cr to a SAC105 alloy with 0.1% Ni. Other elements that have been added to improve properties include Bi, Co, In, and Ge.



**Figure 10.** Addition of 0.03% Cr improves the mechanical shock performance of SAC 105 + 0.1Ni alloy. After Pandher et al. [4].

Various reasons have been cited for the improved mechanical shock performance of low Ag and doped SAC alloys, particularly on copper surfaces. For example, Pandher et al. [4] provided data showing that microalloying additions slow inter-diffusion, thus reducing IMC thickness or propensity for void formation. Further, they showed that small amounts of Ni can decrease Cu<sub>3</sub>Sn IMC growth, improving reliability (Fig. 9). Finally, these authors noted

that low Ag content will decrease the strength and elastic modulus of the solder, transferring less stress to the solder/substrate interface compared to a high Ag alloy. Similarly, work at Intel emphasized that low elastic modulus and low yield strength improves the mechanical shock resistance of low Ag alloys, and that optimization of these properties requires increasing the amount of primary Sn relative to the  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  phases in the alloy [19,21]. H. Kim et al. [19] also found that the majority of cracking in SAC405 solders was through the IMC layer (package side). Cracking in the SAC105 joints was more complex, with cracks going through the bulk solder near the IMC layer and in the IMC. Pandher et al. [4] found that when small amounts of Cr and Ni are combined in low Ag alloys the occurrence of flat, brittle interfacial fractures (Mode 4) are reduced 80% compared to the base alloy without additives.

Syed et al. [20,23] provided one note of caution when making conclusions regarding mechanical shock performance of various alloys: the effect of solder pad surface finish. They found that SAC125 + Ni did not produce a significant drop/shock performance improvement over SAC305 for Ni/Au package finish (and Cu-OSP PCB finish). However, this alloy was the best performer for Cu-OSP finish on both the package and the PCB. Other literature data also indicate a strong dependence of mechanical shock performance on pad finish [24,25].

Still, it now appears clear that reduced Ag content solder ball alloys improve mechanical shock performance over near eutectic alloys with Ag content  $\geq 3\%$ .

### IMPACT OF LOW Ag BALLED BGA COMPONENTS ON PCA MANUFACTURING

Although low Ag BGAs have been successfully integrated into the many products today, issues have surfaced when attempting to use them in either more thermally challenging assemblies or if having to use them in a backwards compatibility scenario where they are being soldered to the PCB using Sn/Pb solder.

#### Thermally Challenging Assemblies

With the potential benefits of alternate alloy balled BGA components come some associated impacts to the manufacturing process, specifically if having to incorporate them into a more thermally challenging assembly. To understand the issue better, the impact of alloy composition on melting point needs to be understood. Figure 11 depicts the melting point of several common SAC alloy compositions (note: the temperatures depicted on the graph represent the points at which the full liquid phase exists).

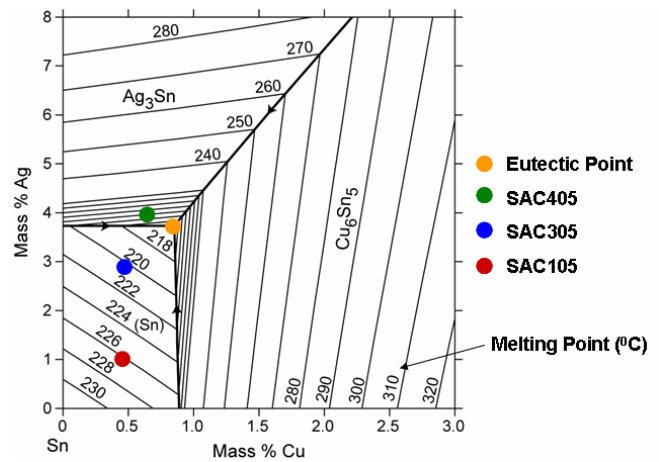
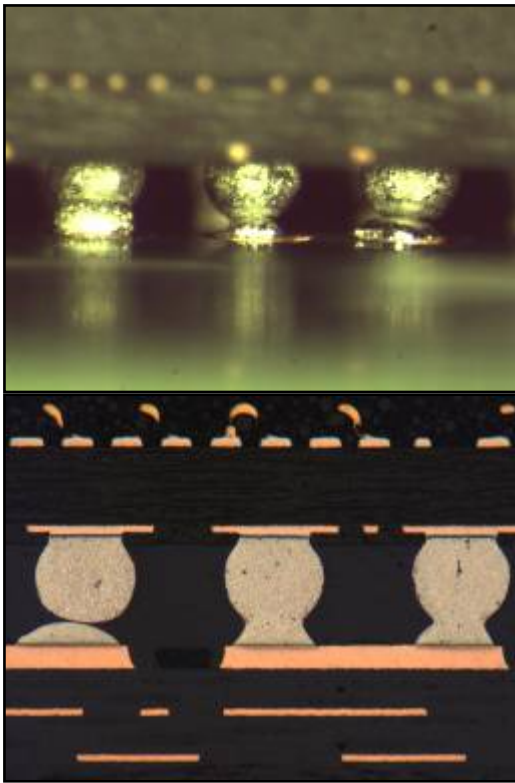


Figure 11. SAC Phase Diagram

The addition of other alloying elements meant to affect undercooling, formation of various intermetallics, matrix properties and microstructure may also impact the melting behavior of the alloy. Such changes can increase the melting point of the solder ball by as much as  $10^\circ\text{C}$  over that for SAC305 or SAC405 ball compositions. In many cases, either not all suppliers on the approved vendor list (AVL) for a package have a consistent ball composition and the supplier has made a change in the composition and not changed either the marking or part number of the package to indicate such. This situation can impact the assembly yields, or worse yet, create unacceptable solder joints because the assembly was soldered at too low a temperature. Improperly assembled components, such as those shown in Fig. 12, are a significant reliability risk, since they may pass electrical test but fail more rapidly in the field than a properly formed solder joint. The obvious solution would be to simply raise the assembly temperature of all Pb-free products from the current minimum peak temperature of  $230\text{--}232^\circ\text{C}$  by approximately  $5\text{--}7^\circ\text{C}$ . This might be practical for simple, less thermally challenging products where the range of package types drives a low thermal gradient and none of the parts exceed the maximum allowable body temperatures as specified by J-STD-20. However raising the soldering temperature on more thermally challenging products can be next to impossible without running the risk of overheating certain packages on the board. Increasing temperatures will also put more strain on the PCB laminate, as well resulting in potentially more warpage or increasing the likelihood for pad cratering. Profiling studies appear to suggest that 1% Ag alloys are incompatible with any current industry Pb-free assembly specification that requires a minimum reflow peak temperature and time above liquidus (TAL) of  $230^\circ\text{C}/60$  sec. This could preclude their use on thermally massive components on thermally challenging assemblies.

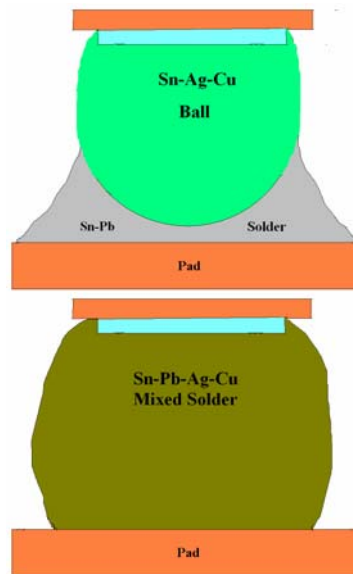


**Figure 12.** Unmelted Solder Balls and Unacceptable Solder Joints [22]

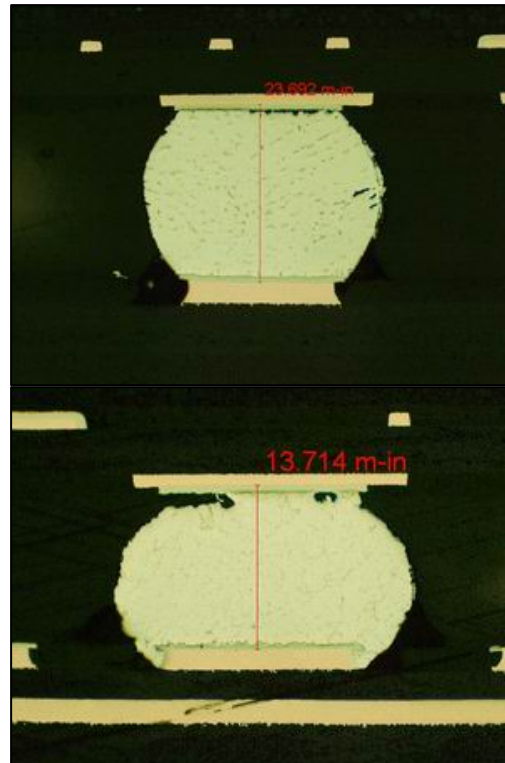
### Backwards Compatibility

Not all products produced today are manufactured using Pb-free solders. Those OEMs that qualify for exemptions specified in the RoHS Directive are still assembling many of their products using Sn-Pb solder pastes. The challenge for these OEMs has been a shrinking supply of Sn-Pb balled BGAs, especially if the part is also used by OEMs building products for consumer applications where no exemption for Sn-Pb solder exists. In some cases, the use of Pb-free balled BGAs is the only available option. The only recourse is to use the Pb-free BGA in a Sn-Pb soldering process. Previous reliability studies on backwards compatibility conducted using SAC305 and SAC405 BGAs soldered using Sn/Pb paste have demonstrated that by soldering at peak temperatures in excess of 217°C, Sn-Pb solder paste and SAC BGA balls mix completely to form a homogenous microstructure with adequate reliability performance for most electronic applications, Fig. 13.

However, the introduction of lower Ag content balled BGA components has changed this situation, particularly for rework operations. Unlike SAC305 or SAC405 BGAs, when SAC105 BGAs are reworked with Sn-Pb solder paste, severe voiding can occur at the component to ball interface, as shown in Fig. 14.



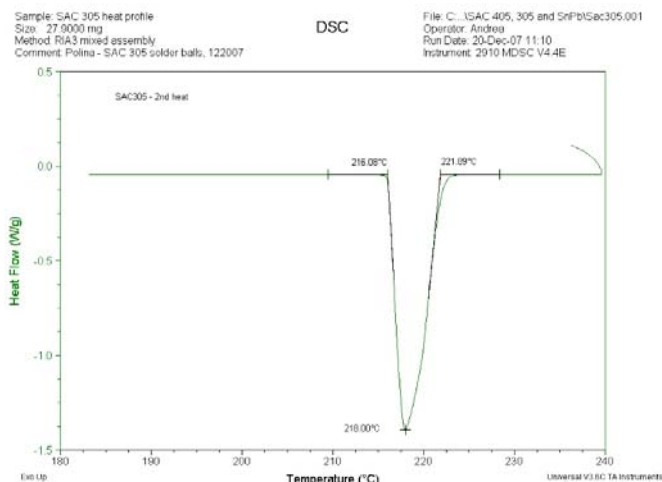
**Figure 13.** Full Metal Mixing after Soldering



**Figure 14.** Voiding Observed after Rework of a SAC105 BGA using Sn/Pb Paste

To understand the root cause of this phenomenon, we need to examine the differences in the composition between the different SAC alloys more closely. The issue with the SAC105 composition is that it is much further from the eutectic point than SAC305 or SAC405. The eutectic composition for the SAC alloy was determined through experimentation conducted by the National Institute of Standards and Technology (NIST) to be 95.6%Sn, 3.5%Ag and 0.9%Cu. Therefore, both SAC305 and SAC405 are

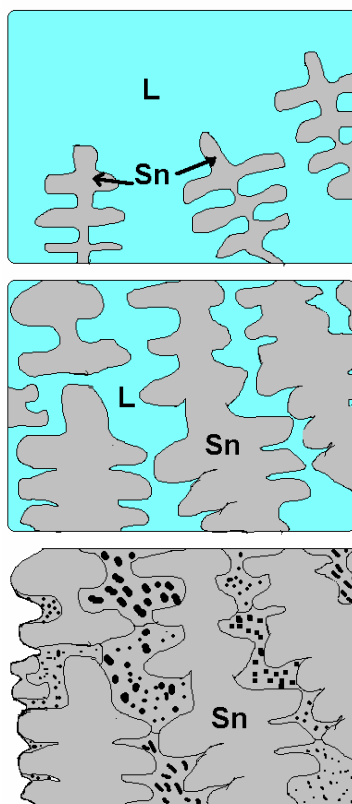
closer to the eutectic point than SAC105 due to the difference in the Ag content, as was shown in Fig. 11. From this phase diagram, it can be observed that the minimum melting temperature for the eutectic composition is 217°C. For all other compositions the melting temperature is higher. Additionally, when a non-eutectic alloy solidifies, instead of all constituents crystallizing simultaneously, a phased solidification occurs, with one component of the alloy crystallizing at one temperature and the other(s) at a different temperature; i.e., a “pasty” range occurs. For the SAC alloy these different phases include: Sn, Ag<sub>3</sub>Sn, Cu<sub>6</sub>Sn<sub>5</sub> and the ternary eutectic itself. The phase transformations that occur while freezing can be determined through differential scanning calorimetry (DSC). DSC can be used to find the solidus (freezing point) and liquidus (melting point) temperature of any metal alloy or complex mixture. Figure 15 shows the DSC curve for SAC305, indicating a melting point of 218°C and a fairly small “pasty” range (i.e. from 216°C to 221°C) since it is close to the eutectic composition.



**Figure 15.** DSC Curve for SAC305 Alloy

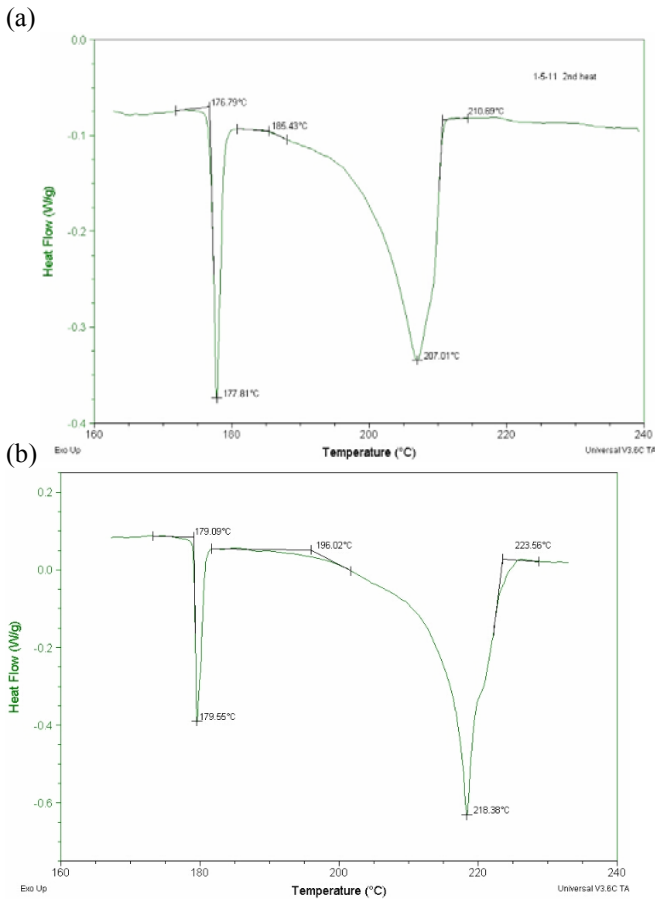
Figure 16 shows the typical solidification sequence for a SAC alloy. Sn will normally solidify out of solution first followed by either Ag<sub>3</sub>Sn or Cu<sub>6</sub>Sn<sub>5</sub> and last the Sn-Ag-Cu eutectic phase.

To better understand the differences in microstructure formation during solidification of SAC105/Sn-Pb vs. higher silver content BGAs, DSC analyses were performed on SAC305/Sn-Pb and SAC105/Sn-Pb combinations. The representative curves are shown in Fig. 17.



**Figure 16.** Solidification Behavior of Non-Eutectic SAC Alloys

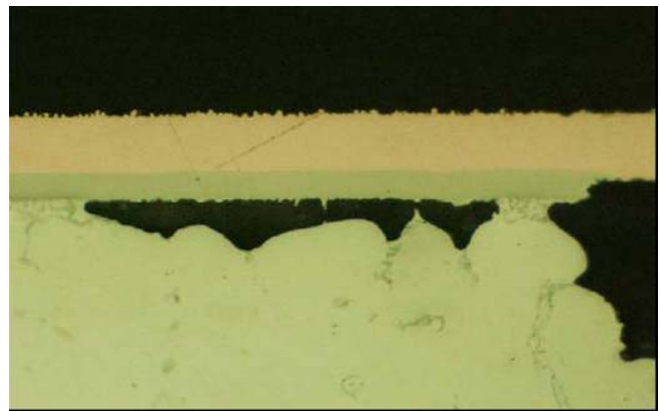
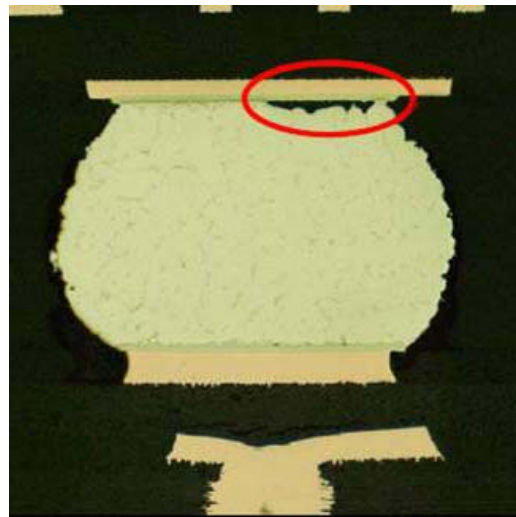
When a SAC105 ball is mixed with Sn-Pb eutectic solder paste, the resulting alloy has a very wide “pasty” range of approx. 45°C (177°C to 224°C) compared to that of the SAC305/Sn-Pb combination (approx. 30°C). The extra 15°C are the result of the additional Sn in the SAC105 versus the SAC305, driving up the overall melting point of the alloy and resulting in more time being required for the solidification of certain constituents. For example, Sn will need more time to solidify in the SAC105 case than the SAC305 case, resulting in much larger Sn dendrites. The multiple troughs from the DSC curves also reveal the various phases that solidify. For example, 179°C is the melting temperature of the ternary Sn-Ag-Pb eutectic that forms in the last portions of the liquid solder. Note that the curves presented are for “pure” SAC/Sn-Pb solder combinations. In real life soldering situations, the presence of additional alloy dopants (e.g., Ni, Mn, Bi, Ce etc.) or constituents resulting from the dissolution of substrate material, such as organic and inorganic additives that were co-deposited with the PCB surface finish, can lower the final solidification temperature even further.



**Figure 17.** DSC Heating Curves for (a) SAC305/Sn-Pb and (b) SAC105/Sn-Pb Alloys. Data from ref. [26].

During BGA rework, heat is primarily applied unidirectionally from the top of the component by the rework nozzle while heat is dissipated through the colder PCB. This results in a temperature gradient across the solder joint with the top (component) side being hotter than the board side. Solidification therefore begins on the board side of the solder joint and progresses to the component side, following the DSC curve. This results in more pronounced phase segregation than generally observed during primary attach, as can be observed in Fig 18.

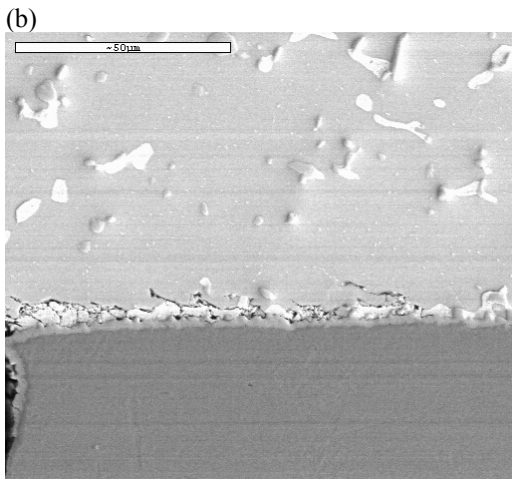
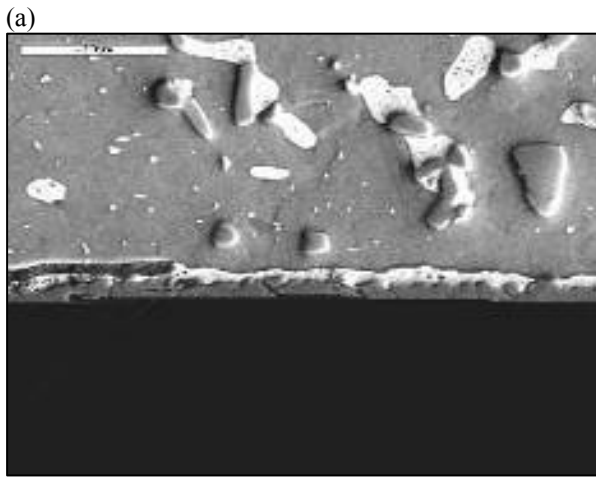
As the Sn dendrites grow towards the hotter component side, the liquid is depleted of Sn and enriched with Pb and Ag. The remaining liquid crystallizes as binary and then ternary eutectic in the remaining interdendritic spaces. As most of the solder joint is already solid, the contraction forces also play a significant role in opening the gap through the liquid layer. The last portion of the liquid will finally solidify as a ternary Sn-Ag-Pb eutectic on the component side when the temperature of that region reaches about 177°C. A closer look at the Fig. 18 reveals the eutectic layer at the pad/solder interface (lower image). Note also that the separation / void has a Sn dendrite shape indicating that it is formed due to shrinkage and not some other process issue.



**Figure 18.** Shrinkage Voids and Low Melt Eutectic Concentration from Repairing SAC105 Ball with Sn/Pb Paste [26]

Although primarily a rework issue, such voiding may also occur during the assembly of high density, thick boards or whenever uniform heating of the assembly is a challenge. Figure 19 provides examples where the low melt accumulation is evident on the board side of the solder joint. The accumulation of low melt eutectic and shrinkage voiding leads to a weakened interface from a thermomechanical strength perspective. Cracks can be seen propagating along the low melt and bulk solder interface in Fig. 19(b).

In summary, the new alloy alternatives add complexity to the challenge of processing thermally challenging PCAs and with mixed SAC/Sn-Pb alloy assemblies.



**Figure 19.** Low Melt Accumulation and Crack Propagation: (a) – Ref. [27], (b) – Ref. [26].

## STANDARDS

There are a number of key industry standards that require updating or modification to address the new Pb-free alloys. The iNEMI Alloy Alternatives team is helping to drive these changes, where possible.

First, the iNEMI team has provided input to the IPC/JEDEC committee to provide guidance on J-STD-609, “Marking and Labeling of Components, PCBs and PCBAs to Identify Lead (Pb), Pb-Free and Other Attributes.” There is confusion regarding how to label low Ag and microalloyed materials. The committee is currently considering our proposal to provide clarification on labeling for the new alloys.

Second, the iNEMI team presented to the JEDEC JC-14 committee our concerns about part numbers and customer notification when BGA/CSP suppliers change ball alloys. We noted that a Pb-free BGA ball alloy change may have an impact on printed circuit assembly (PCA) manufacturing due to the higher melting point of some alloys, as discussed in the previous section. In particular, the change to low Ag ball alloys may require a change to PCA manufacturing processes. Our request was that the committee consider

mandating, or at least recommending, that new part numbers be issued when a BGA supplier changes the solder ball alloy such that a manufacturing process change is needed. A new task group was formed to consider this issue, our recommendation, and other related topics for standardization by JEDEC.

Another standard being discussed by the iNEMI team is J-STD-006, “Requirements for Electronic Grade Solder Alloys and Fluxed and Non-Fluxed Solid Solders for Electronic Soldering Applications.” Our goal is to update J-STD-006 to account for new alloys, particularly those with microalloy additions. Presently, some microalloying elements are present in amounts that would normally be considered an impurity. We have communicated our concerns to the committee responsible for this standard, and will be working with them to update the document.

## ALLOY DATA REQUIREMENTS

One situation that creates uncertainty in the industry regarding new alloys, and which may slow the adoption of improved materials, is the lack of defined information requirements for alloy acceptance. The acceptability of any alloy may vary from product class to product class, and possibly from company to company. However, the methodology and data requirements may be largely same, regardless of product requirements or company.

Thus, the iNEMI Alloy Alternatives team is examining the possibility of establishing a set of data requirements and the methods to generate these data. Ultimately, the goal would be to take this approach to the relevant standards bodies for industry acceptance and standardization. Currently, the team is assessing the possibility of following the approach published by Hewlett-Packard at this conference [28], at least as a starting point.

## KNOWLEDGE ASSESSMENT

The efforts of the iNEMI Alloy Alternatives team so far have been focused on establishing (and now communicating) the industry state of knowledge regarding new Pb-free solder alloys. Table 3 summarizes the major areas where industry understanding is relatively complete, or at least adequate. A summary of key knowledge gaps is provided in Table 4.

The iNEMI team is now focused on addressing the key knowledge gaps to further the industry’s understanding of the benefits and possible risks of new Pb-free solder alloys. Follow-on activities are being planned that will add value to the industry and avoid redundancy with other efforts. In addition, the team continues to engage standards bodies in the creation or updating of standards that will help the industry to manage the increasing number of alloys choices. The goal is to drive standards that will help companies take advantage of the benefits of new alloys without suffering unintended negative consequences.

**Table 3.** Areas where knowledge is complete/adequate.

| Sufficient Knowledge   |
|--|
| Low Ag alloys improve drop/shock resistance  |
| Micro alloy additions significantly improve drop/shock performance on Cu surfaces but not on Ni surfaces |
| Decreasing Ag content decreases elastic modulus, yield and tensile strength of SAC                       |
| Decreasing Ag content decreases creep strength of SAC  |
| Alloy additions can increase the creep strength of low Ag SAC alloys                                     |
| SAC alloys are not inherently brittle (needs to be better communicated, however)                         |

**Table 4.** Key knowledge gaps regarding the performance and impact of new Pb-free alloys.

| Gap or Concern   |
|--|
| <b>High Priority</b>   |
| Advantages and disadvantages of specific alloys  |
| Composition limits for microalloy additions; ranges of effectiveness   |
| Standard method to assess new alloys; standard data requirements   |
| Consistency of testing methods, including test vehicles & assembly, test parameters, etc.                          |
| Establish the microstructural characteristics of specific alloys   |
| Long term reliability data for new alloys, particularly low Ag & microalloyed                                      |
| Lack of thermal cycle data for evaluating new alloys; benchmark to Sn-Pb and SAC 305/405                           |
| <b>Medium Priority</b>   |
| Assessment of new alloys for use in "mission critical, long life" products   |
| Impact of rework on microstructure and properties  |
| Mixed Sn-Pb/Pb-free assembly, including rework   |
| Impact of alloy composition on work hardening rates & other flow properties; effect of strain rate and temperature |
| Impact of alloy composition on bend/flex limits (moderate strain rate; ICT, handling, card insertion, etc.)        |
| Thermal fatigue accelerations factors (not yet fully established for SAC 305/405)                                  |
| Impact of aging on microstructure and mechanical properties  |
| <b>Low Priority</b>  |
| Solder process margins required for new alloys used in various product classifications                             |
| Mixing of different BGA ball alloys and paste alloys for various component and board designs                       |

### SUMMARY AND CONCLUSIONS

The knowledge assessment efforts of the iNEMI Alloy Alternatives team have been described. This multi-company, multi-sector team has assessed the recent literature regarding new Pb-free solder alloys alternatives and come to the following conclusions.

1. Considerable progress has been made in understanding the fundamental relationships between alloying elements and properties for the SAC family of new Pb free solders. Additional work is needed to fully characterize the complex microstructures and their influence on physical and mechanical properties.

2. Areas where the performance of new alloys is reasonably well established have been identified. Some of these include: (i) impact of Ag content and microalloy additions on mechanical shock reliability; (ii) impact of Ag content on elastic stiffness, plastic flow and creep behavior of SAC alloys.

3. Areas where more knowledge is needed in order to properly assess the benefits and potential risks of new alloys also have been identified. Some of these include: (i) thermal fatigue performance, including the impact of microalloy additions and development of acceleration models; (ii) the impact of alloy composition on the full range of solder processes; (iii) impact of thermal aging on microstructure and properties; (iv) impact of composition on bend/flex limits related to PCA manufacturing, test, board handling, etc.

4. Standardized data requirements for assessment of new alloys are needed so that each company can compare alloy performance with product requirements over the full range of relevant properties. The iNEMI Alloy Alternatives team is currently considering the HP approach as a starting point for such standardization.

5. The iNEMI Alloy Alternatives team is actively engaged with relevant standards bodies to create or update industry standards related to new Pb-free solder alloys.

### ACKNOWLEDGEMENTS

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