Alternative Pb-free Soldering Alloys

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ABSTRACT

This paper discusses a variety of alternative Pb-free soldering alloys, including the mainstream SAC305, and compares them against the benchmark eutectic SnPb solders. These alternative alloys were developed for several reasons: low temperature processing, low cost, high mechanical shock resistance, and high thermal cycling performance, as well as replacing high lead content interconnections (component package die-attach applications). These alternate alloys offer significant reliability improvements and address the specific challenges with SAC, such as high processing temperatures, voiding, wetting, fragility, and the high cost of silver. Several alloys show promise as replacement materials for targeted product applications. These include SnBiAg and SnInX for low processing temperatures; SACM™ and SACTi for superior drop shock and good thermal cycle performance; BiAgX™ for high temperature die-attach applications; and Sn992 and Sn995 with the addition of Bi and Co for low cost soldering. This paper will focus on the work done with a low Ag SAC doped with Mn (SACM™), especially as it relates to drop shock and thermal cycling performance. It will also discuss the potential high lead-containing replacement alloy, BiAgX™, as a substitute for high temperature die-attach interconnections in component package applications.

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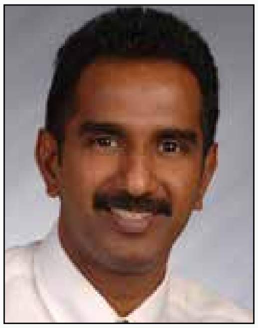

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In the early 2000s, as electronics manufacturing began to transition to Pb-free soldering materials in response to the new RoHS requirements, a variety of Pb-free alternatives were proposed. At that time, the majority of the industry settled on SnAgCu alloys. By 2008, the most common alloy being used was SAC305, which has a composition of 96.5%Sn/3.0%Ag/0.5%Cu. Even though this alloy has been used successfully, it has several disadvantages which hampered its adoption. One was the fragility of solder joints in drop shock testing relative to 63Sn/37Pb, and another was the high cost of Ag. Good drop shock resistance is especially critical for portable devices employing area array packages such as BGAs and CSPs. Reducing the silver content to 1.0 percent dramatically improved drop shock performance, but reduced thermal cycle performance. There are a number of alternative alloys that have been developed, some in use within the industry, to address these challenges. However, there is no single drop-in solution when it comes

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to alloys. The needs for microelectronics and electronics assembly are broad and it is unlikely that a single alloy can meet all their requirements. Therefore, it is important to understand the alloy differences and their impact on the assembly process and reliability. The Pb-free options for high temperature soldering (above 260°C) are still undetermined as the RoHS deadline for removing lead from these types of solders approaches. Alternative high-temperature lead-free (HTLF) solders designed to replace the conventional high lead-containing alloys, i.e., Pb5Sn and Pb5Sn2.5Ag, are still far from mature. Although there is no drop-in replacement for HTLF solders, BiAgX™ has proven to be an alternative and potential solution for the die-attach applications.

Selection of SAC305 and its challenges

In preparation for the implementation of RoHS in 2006, there were several solder alloy candidates that were offered as potential replacements for the SnPb standard. A critical factor in the selection process was the melting temperature of the alloy. Table 1 shows the alloy candidates and their melting temperatures as compared to SnPb.

Alloy	Melting Temp (°C)
Sn63Pb37	183
Bi58Sn42 (BiSn)	138
Sn77.2In20Ag2.8	187
Sn96.5Ag3.5 (SnAg)	221
Sn99Cu1 (SnCu)	227
Sn96.5Ag3.0Cu0.5 (SAC305)	217
Sn95.5Ag3.8Cu0.7 (SAC387)	217
Sn95Sb5 (SnSb)	240
Sn91.8Bi4.8Ag3.4	213

Table 1. Melting temperatures for several Pb-free candidates.

The melting temperature of BiSn was considered too low, and SnSb and SnCu were considered too high. These three candidates were eliminated early in the process. The remaining alloys were selected and considered as possible alternatives based on their applications. SnInAg was sidelined because of its higher cost. SnBiAg had the most potential with acceptable soldering performance; however, bismuth (Bi) is not compatible with lead. When Pb is mixed with Bi, there is a potential to form a low melting phase of SnPbBi which melts at 96°C. Since there were several mixed applications (e.g., lead-free and leaded solders) in the early transition, this alloy was also considered unacceptable. This situation led the industry to choose SnAgCu (SAC) as the solder alloy of choice for SMT. Originally, there were three variations of SAC that were short listed: SAC305, SAC387, and SAC405. In the end, SAC305 was chosen due to its lower Ag content and lower cost. The lower Ag content also exhibited a lower tombstone rate as shown in Figure 1.

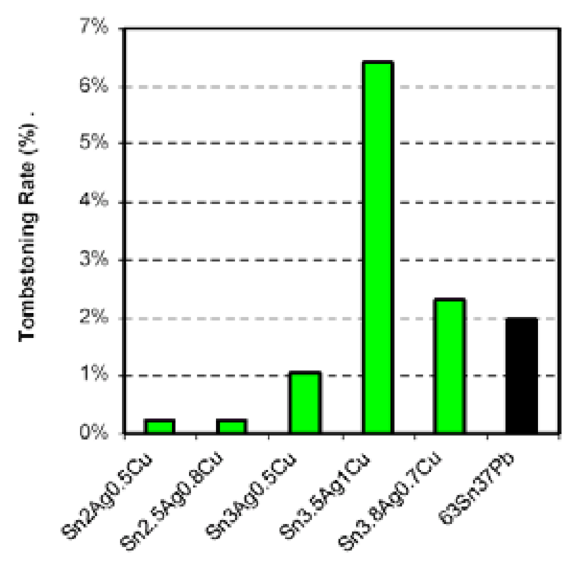


Figure 1. Tombstoning rate of various SAC alloys compared to SnPb.

Even though the alloy selected for SMT assembly was SAC305, it had its own challenges. The major challenges were the higher melting temperature and the industry's convergence towards miniaturization assemblies. The higher reflow temperature put a significant amount of stress on the components, board, and process. Board delamination or conductive anode filament [1] and component (BGA) warpage saw an increase. Figure 2 shows the rate of warping under increasing temperatures.

Transitioning to Pb-free solders seemed to be faced with significant risk of solder joint fragility associated with all the commonly used solder pad surface finishes [2]. Figure 3 shows that SAC alloys are more fragile under high strain conditions compared to the standard SnPb. The higher the Ag content, the harder the alloy, making it more prone to brittle fracturing during mechanical shock, as shown by the cyclic shear strain range for SnPb versus SAC in Figure 3. However, Pb-free reliability is not an A-B comparison to SnPb. It strongly depends on the component type, assembly process, test conditions, and the solder alloy. [3]

Aside from other process challenges, such as wetting ability and voiding under higher temperatures, the cost of SAC, especially Ag, has seen significant increases in recent years. These conditions have driven some companies to look for alternatives to SAC. Figure 4 shows the cost trend for SAC305 and the volatility of metal prices.

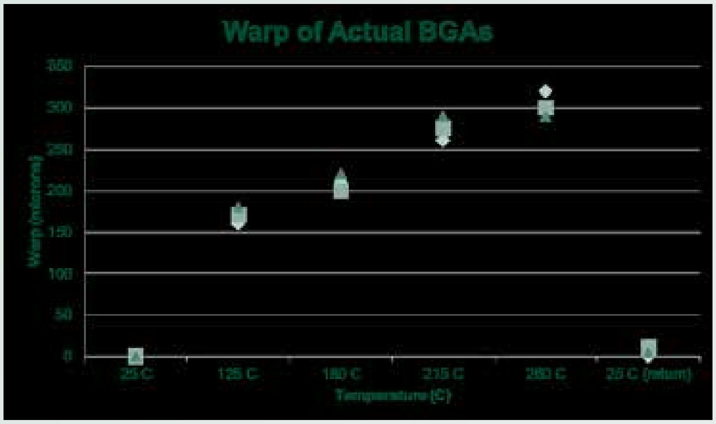


Figure 2. BGA warpage over temperature.

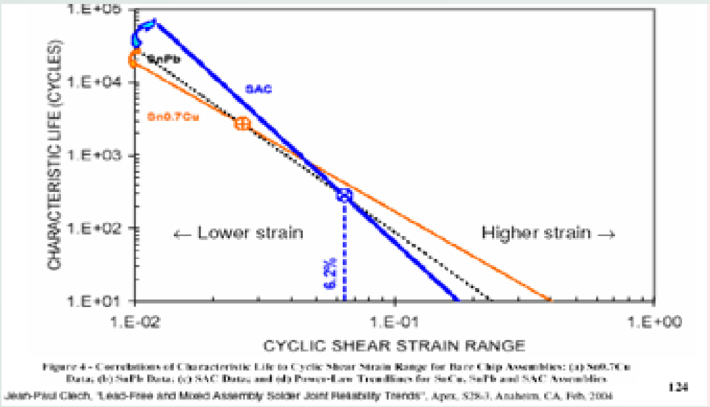


Figure 3. Correlation of characteristics life to cycle shear strain range for bare chip assemblies. (Jean-Paul Clech,"Lead-free and Mixed Assembly Solder Joint Reliability Trends", APEX S28-3, Anaheim, CA Feb 2004.)

Figure 4. SAC305 cost trend from Aug '10 to May '13.

Low melting temperature options

A low temperature solder is advantageous because the lower temperature thermal processing requirements can reduce thermal damage caused by higher melting temperature alloys. Defects, such as delamination or "pop-corning" of moisture-sensitive devices (MSD), can be minimized or eliminated by using lower temperature solders. Delamination or pop-corning failure modes occur when moisture diffuses into the plastic components; this moisture then rapidly expands upon heating. Lower temperature alloys may also be considered for use with temperature sensitive components or step soldering or rework processes. Two alloy candidates that are widely used and considered for low temperature Pb-free soldering are 58Bi/42Sn and 57Bi/42Sn/1Ag. 58Bi/42Sn has a eutectic melting temperature point of 138°C. The wetting performance is comparable to SnPb both in air and nitrogen reflow on various surface finishes. The addition of silver to SnBi makes the solder alloy more ductile and enhances the thermal fatigue life compared to eutectic BiSn. The 57Bi/42Sn/1Ag alloy has a melting temperature range of 139°C -140°C. The application of low-temperature solders in SMT assembly processes for products that do not experience a harsh temperature environment is technically feasible. Low-temperature assembly is a promising way of increasing process flexibility and component reliability. This low-temperature option is suitable for heat-sensitive components and for applications that require lower operating temperatures. Low reflow temperatures offer the opportunity for lowest overall cost of the PCB, components, usage of reflow equipment, and process. Figure 5 shows the typical profile used for low melting temperature alloy and the wetting appearance of the solder. [4]

There are some concerns with bismuth-containing alloys, as Bi tends to be fairly brittle. Hence, these alloys are not at all suitable for devices that will experience drop shock, such as mobile phones. However, bismuth-containing alloys perform well in applications that require good thermal cycle performance, such as servers, main frame computers, and other stationary devices. Bismuth and bismuth-containing alloys are unique in that they expand upon cooling, which can cause issues such as fillet lifting with through-hole components, and if used in an application where lead is present, bismuth can form a low-melting eutectic at 96°C. This concern was a real issue when the industry first transitioned to the lead-free because most assemblies were only partially lead-free and lead contamination was a real concern. As the transition has progressed, this situation has become much less an issue. Hewlett Packard (HP) has done an extensive study on

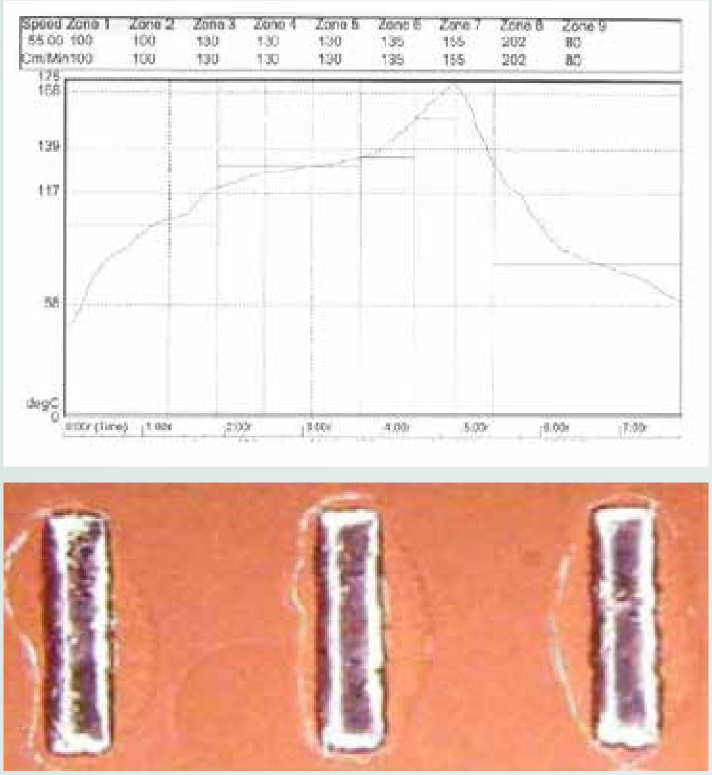


Figure 5. BiSn reflow profile and solder wetting appearance.

this low melting temperature alloy [7]. The HP study found that BiSnAg had higher shear strength than SnPb at 20°C, comparable shear strength at 65°C, and lower, but comparable, shear strength than Sn63 at 110°C.

Low cost - no silver (Ag) options

A low-cost alternative to near-eutectic SAC alloys for Pb-free assembly is important for producing affordable electronics products. Metals prices, especially silver, have been a concern for many manufacturers. High Ag-containing SAC alloys, such as the SAC305, SAC387, and SAC405, are still dominant when it comes to thermal cycling reliability, while the low Ag-containing SAC alloys, such as SAC105 and SAC0307, were preferred for drop shock resistance. The low Ag-containing alloys had poor wetting performance, in addition to reduced thermal cycling performance. To compensate for tradeoffs in performance, dopants were introduced as a way to improve properties such as wetting, appearance, and reliability, and yet maintain similar reflow characteristics. It seemed that each supplier has its own variation, such as SN100C, SACX, SACM™, and Sn992. Each of these alloys has a different mix of dopants and, it is suggested, slightly different levels of performance, although it is difficult to characterize how much.

The Sn992 alloy contains 99.2%Sn/0.5%Cu/0.3%Bi+Co. Several initial experiments on wetting behavior and IMC formation show promising results for this alloy even though more reliability testings are needed. Figure 6a and Figure 6b show the wetting comparison between Sn992 and the high Ag-containing SAC387. This comparison was made with the same flux vehicle, metal load, and powder size with new and oxidized boards, and then reflowed with the same ramp-to-peak reflow profile (peak 240°C). The solder coalescence and spread was observed [8] using a DSC. The melting temperature of Sn992 is 227°C. Will alloys with such varying melting behaviors form a good solder joint with the same reflow profile? Another experiment was conducted where Sn992 was printed and reflowed with QFN components on test boards with copper pads finished with OSP under the same processing conditions as SAC solders. The QFN was cross-sectioned and etched to look at IMC thickness directly after reflow.

Figures 7a,7b,7c, and 7d are SEM images comparing the IMC layer of SAC305 to those of SAC105, SAC0307, and Sn992. Despite inherent differences in microstructure for each alloy, IMC layer formations seem to be of a similar thickness, on the order of 1μm [8]. It was also found that a small addition of bismuth did not affect the melting point significantly as shown in Figure 8. Bismuth increased the wetting of Pb-free assembly by breaking up Sn dendrites and promoting a refined grain structure. The initial tests show that even without silver, a similar process performance can be achieved, however, more work needs to be done relating to in-service performance of this alloy. Nevertheless, this option is available for low cost products with minimal reliability requirements.

Figure 6a. Wetting pattern for SAC387. Figure 6b. Wetting pattern for Sn992.

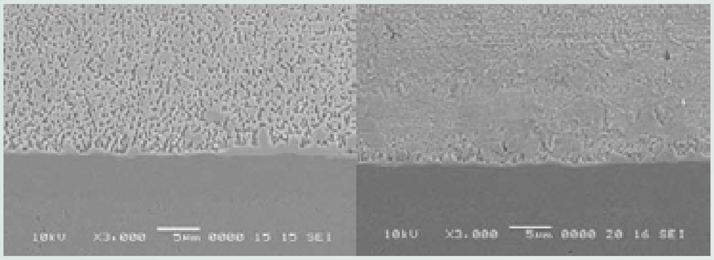


Figure 7a. An etched SAC305 solder joint. Figure 7b. An etched SAC305 solder joint.

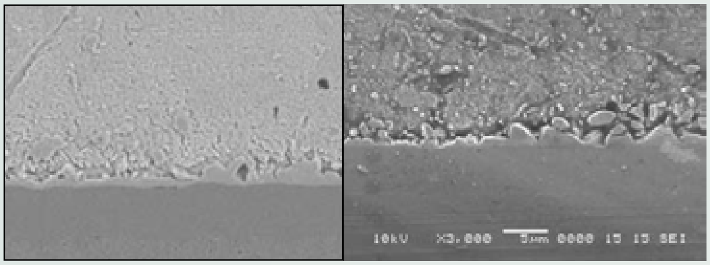


Figure 7c. An etched SAC305 solder joint. Figure 7d. An etched SAC305 solder joint.

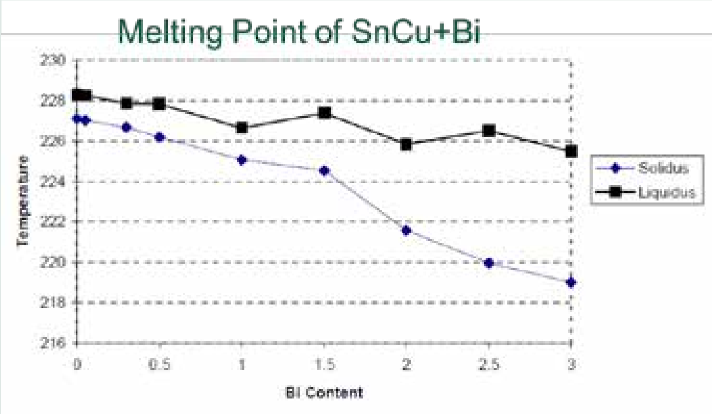


Figure 8. Melting of SnCu with incremental addition of Bi.

Low silver (Ag) options

Based on SAC305 cost and drop shock challenges, low silver solder alloy options within the SAC family are highly desired, especially in mobile device applications. Options were adopted for cost reduction purposes and to avoid the effect of price volatility of silver. The list of alloys is limited, making the search for new alloy development quite challenging. The industry moved to lower Ag-containing SAC alloys like SAC105 (98.5Sn/1.0Ag/0.5Cu) and SAC0307 (99.0Sn/0.3Ag/0.7Cu) because the low Ag content had shown improvement in drop test or mechanical shock performance of the solder joint. However, the downside was that lower Ag-containing alloys have poor thermal cycling performance compared to high Ag-containing alloys. The low Ag-containing alloys also have a melting temperature that is higher by 7°C. Figure 9 shows the limitations associated with adjusting the amount of Ag in the SAC solder alloy. Given the concerns about the fragility of SAC305 and the thermal performance of SAC105, the industry researched further and began adding dopants. SAC105 was used as the base to further improve mechanical shock performance, which was still inferior to SnPb. Several dopant candidates were researched, such as the addition of Bi, Ti, Ce, Mn, AlNi, Ge, and Y [5]. Various combinations and percentage of dopants were studied. An example of the drop test performance for the thermally aged samples of the doped alloys is shown in Figure 10. The drop test results indicate the potential of dopants compared to straight SAC105.

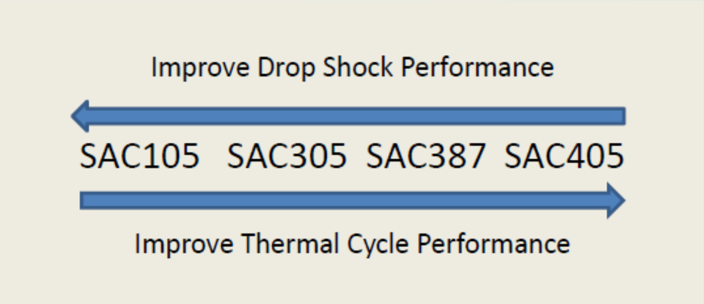


Figure 9. General reliability trend with changes in Ag content for SAC alloy.

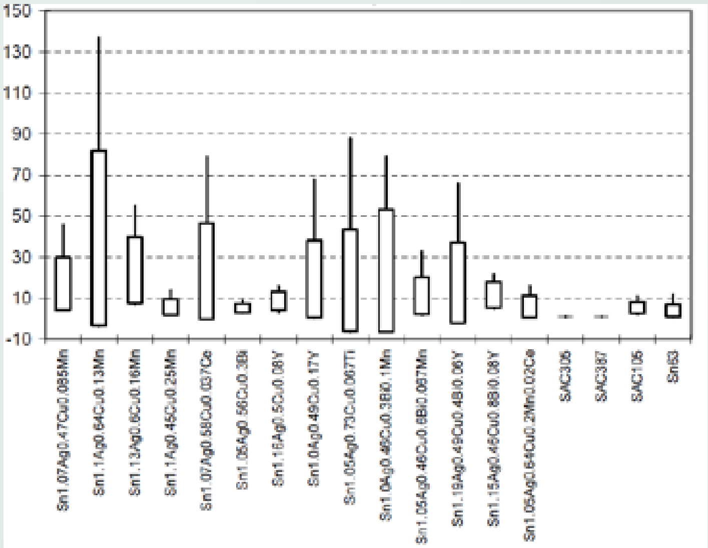


Figure 10. Drop test results of samples after thermally aged at 150°C for 4 weeks.

In this paper we will concentrate on the evolution of SACM™ (SAC + manganese) which has shown significant improvement on both mechanical reliability and thermal performance. SACM™ is an alloy consisting of 0.5-1% Ag, 0.5-1% Cu, < 0.1% Mn. Figures 11 and 12 show the characteristic life (C-life) and first failure in JEDEC Drop Test (JDT) performance for TFBGA (NiAu) on OSP treated PCBs, respectively. Overall, the C-life of alloys for as-reflowed devices is ranked as: SACM > SAC105 > SnPb > SAC305. On the other hand, the ranking of alloys for first failure for as-reflowed conditions is ranked as: SACM > SnPb > SAC105 > SAC305. For devices that have been thermally aged or temperature cycled, the ranking is: SnPb > SACM > SAC105 > SAC305. [6]

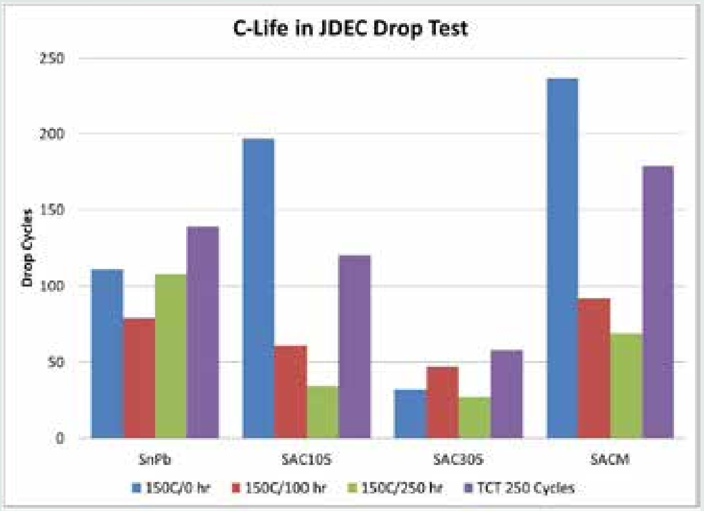


Figure 11. C-life in JDT for TFBGA (NiAu) on PCB (OSP) cycled.

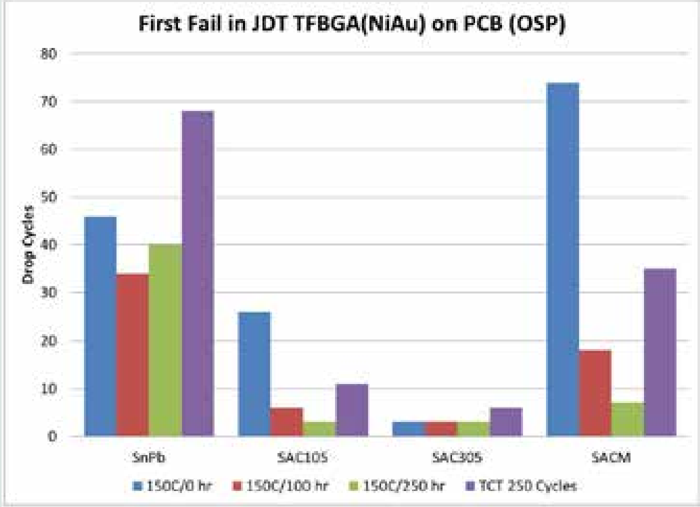


Figure 12. First failure in JDT for TFBGA (NiAu) on PCB (OSP).

(Figures 13 and 14) show the C-life and first failure respectively for TCT. Overall, the C-life of alloys for as-reflowed devices can be ranked as: SAC305 > SACM > SAC105 > SnPb. However, for devices that have been thermally aged or thermal cycled, the ranking of C-life is: SACM, SAC305 > SAC105 > SnPb. The ranking of alloys on first failure for as-reflowed devices is: SnPb > SACM > SAC105 > SAC305. For devices that have been thermally aged or thermal cycled, the ranking of first failure is: SACM > SAC105 > SnPb > SAC305. Although SAC305 has a good C-life, the poor first failure might be a concern for high reliability applications. [6]

SACM™ exhibits a finer and thinner IMC structure at the interface, and the inclusion of dopants in the IMC may also alter the crystallinity, hence, reducing the brittleness of the IMC layer. A stable and fine IMC structure may be the primary contributing factor and the stabilized grain structure that resulted may be the secondary cause for SACM to exhibit a high TCT reliability.

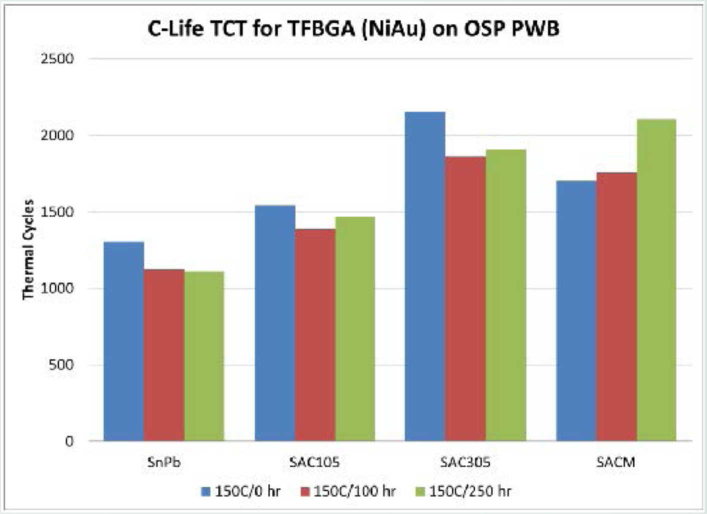


Figure 13. C-life of TCT for TFBGA (NiAu) on OSP treated PCBs

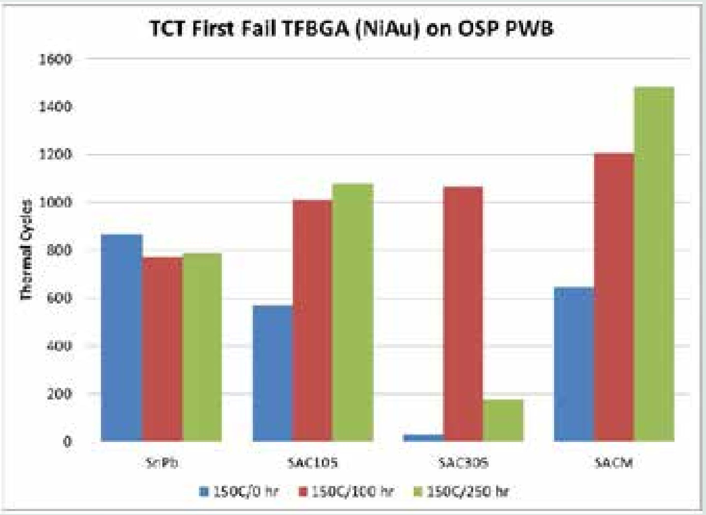


Figure 14. First failure of TCT for TFBGA (NiAu) on OSP treated PCBs.

Figure 15 shows the microstructure of the interface of TFBGA (NiAu) solder joints on OSP treated PCBs aged at 150°C. SACM™ displayed a thinner and smoother interfacial IMC layer than SAC105 at both the package and PCB sides. The mechanism for high drop test performance and high thermal cycling reliability can be attributed to a stabilized microstructure, with uniform distribution of fine IMC particles, presumably through the inclusion of Mn in the IMC. [6]

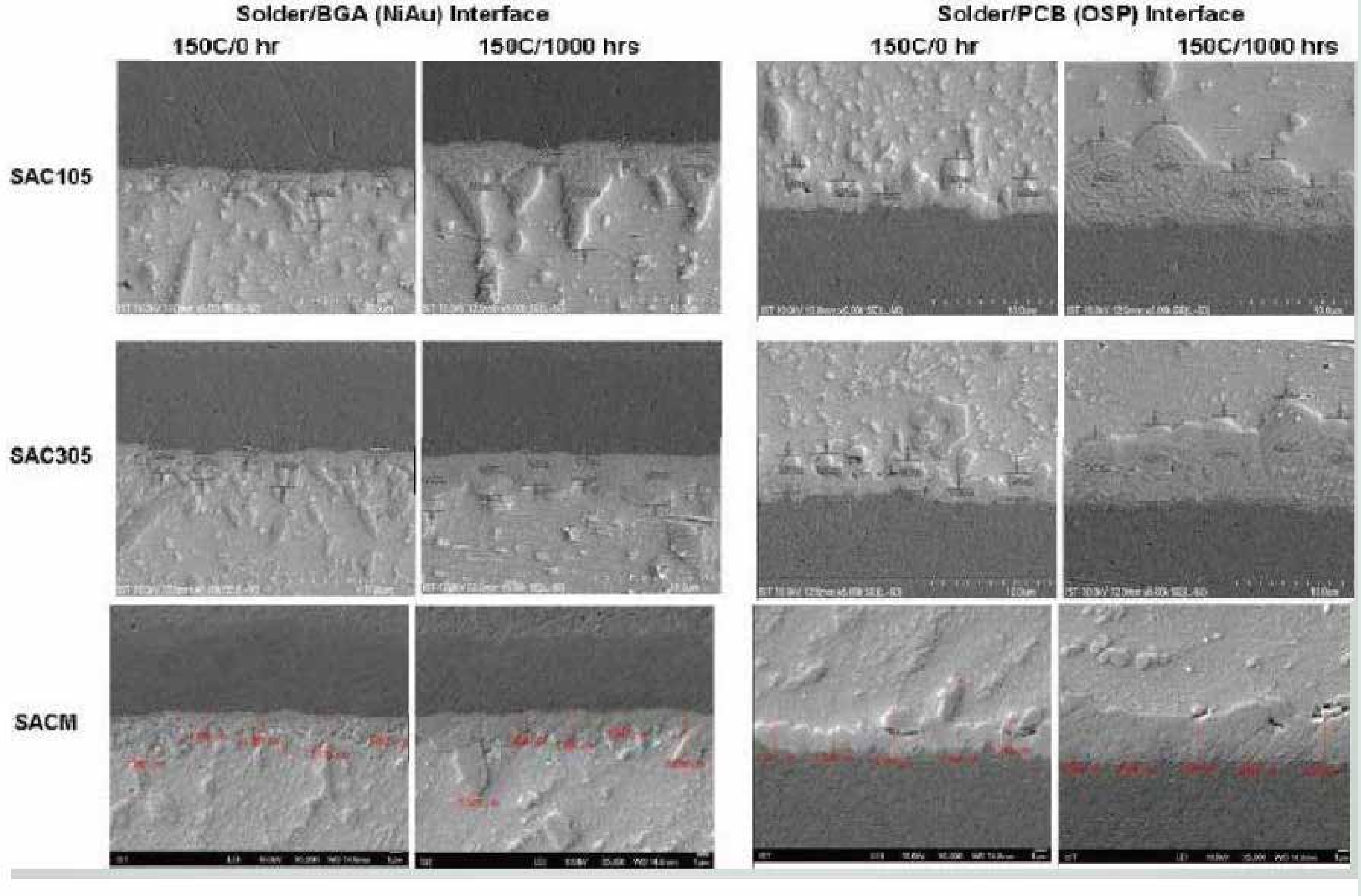


Figure 15. The interface of solder joints of TFBGA NiAu finished solder balls on OSP treated PCB pads aged at 150°C.

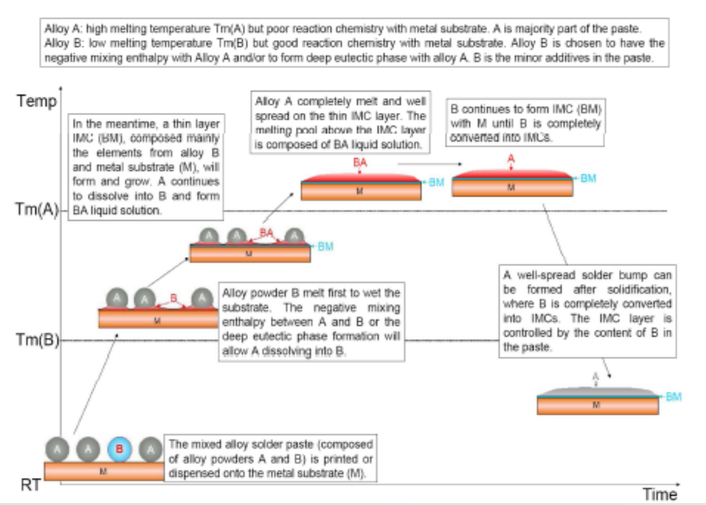
High temperature options

Since 2006, the SMT industry has complied with RoHS and WEEE mainly by eliminating lead as one of the key controlled elements. However, the packaging assembly manufacturers, who use high lead-containing materials, are still exempted from these requirements until year 2014, and may get extended to year 2016. This reason for this is because there is no solution from the industry for a suitable Pb-free alloy to replace the common high lead-containing alloys, such as 95Pb/5Sn and 92.5Pb/5Sn/2.5Ag. Table 2 shows the currently available Pb-free alloys to choose from. Since one of the key requirements for a high temperature alloy is to have a solidus temperature above 260°C so that it can tolerate subsequent SMT reflow up to a peak temperature of 260°C, most of the alloys will not fit as replacement. Except for AuSn derivative alloys, such as the 80Au20Sn, there is no real candidate. AuSn is used in very specific applications, due to very high material costs. BiAg appeared to be a potential alloy as drop in replacement, but the disadvantages of this alloy include low ductility and poor wettability. The industry's requirements were for an alloy with a processing temperature below 400°C, compatibility with mainstream surface finishes, comparable reliability with current high lead-containing alloys, and low cost. A team headed by Dr. Ning-Cheng Lee worked on alloying BiAg with other secondary alloys such as BiSn and developed a mixed alloy power technology called BiAgX™. [9] The mixed alloy powder solder paste technology was invented to efficiently improve the interfacial reaction chemistry. The secondary alloy contains elements which will react relatively aggressively with various surface finish materials, such as Cu, Ag, Ni, and Au during reflow, and provide the wetting required.

standard materials								melting temp deg C	
Sn	Ag	Sb	Au	Bi	Zn	Ge	Al	solidus	liquidus
96.5	3.5							Eutectic	221
65	25	10						Eutectic	233
95		5						235	240
91.5		8.5						248	250
90		10						250	272
	11			89				262	360
20			80					Eutectic	280
					95		5	Eutectic	382
			88			12		Eutectic	356
						55	45	Eutectic	424

Table 2. Standard high temp Pb-free materials and melting temperature.

When soldering, the secondary solder powder will melt earlier than, or together with, the primary solder powder spread on the surface of the bonding parts, and react with the surface finish materials. In this process, the additive solder will dominate the formation of an IMC layer at the interface and the active elements in the additive solder will be completely converted into IMCs (including both the interfacial IMC layer and IMC precipitates in the joint matrix) after reflow. The remaining non-active constituents of the secondary solders will then mix thoroughly with the molten primary solder powder and solidify together to form a homogeneous solder joint. Figure 16 depicts the design idea of this technology. [9]



Alloy A: high melting temperature Tm(A) but poor reaction chemistry with metal substrate. A is majority part of the paste.
Alloy B: low melting temperature Tm(B) but good reaction chemistry with metal substrate. Alloy B is chosen to have the negative mixing enthalpy with Alloy A and/or to form deep eutectic phase with alloy A. B is the minor additives in the paste.

In the meantime, a thin layer IMC (BM), composed mainly the elements from alloy B and metal substrate (M), will form and grow. A continues to dissolve into B and form BA liquid solution.

Alloy A completely melt and well spread on the thin IMC layer. The melting pool above the IMC layer is composed of BA liquid solution.

B continues to form IMC (BM) with M until B is completely converted into IMCs.

Alloy powder B melt first to wet the substrate. The negative mixing enthalpy between A and B or the deep eutectic phase formation will allow A dissolving into B.

A well-spread solder bump can be formed after solidification, where B is completely converted into IMCs. The IMC layer is controlled by the content of B in the paste.

The mixed alloy solder paste (composed of alloy powders A and B) is printed or dispensed onto the metal substrate (M).

Figure 16. Design idea of the mixed solder paste system.

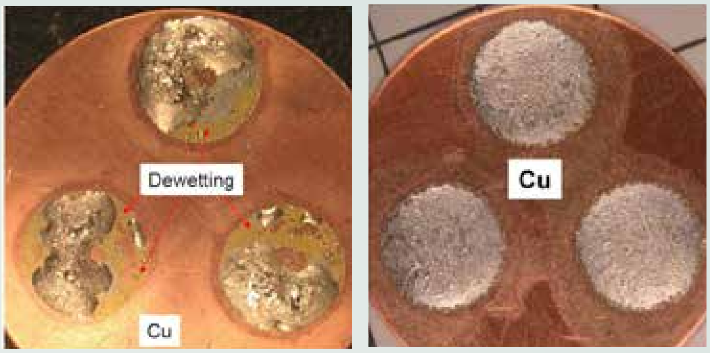


Figure 17a. BiAg wetting on Cu Coupon. Figure 17b. BiAgX wetting on Cu Coupon.

With a properly designed mixed solder paste system, the secondary alloy should not influence the melting behavior of the first alloy.

Figure 17a and Figure 17b shows the wetting appearance of BiAg solder on a Cu coupon compared to the wetting of BiAgX™ solder system. Figure 18 shows the DSC result from a selected BiAgX™ mixed solder paste (BiSn+BiAg+flux). A small melting peak at around 140°C corresponding to the melting temperature of the BiSn phase from the secondary powders is seen, followed by the melting of the first alloy (BiAg) with an onset temperature at 262° C. This observation indicates that there is no eutectic BiSn phases left on second DSC. This means that the reactive element Sn in BiSn is completely converted into IMCs by either forming the interfacial IMC layers with surface finish materials or forming IMCs inside the joint by reacting with Ag from the first alloy, BiAg powder, during reflow.

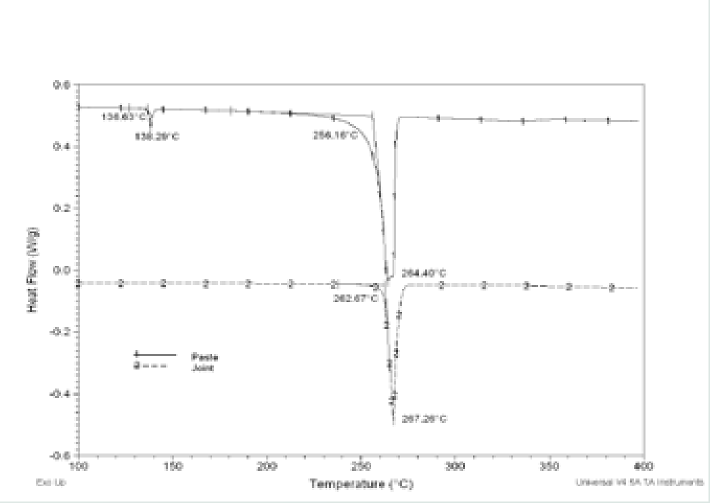


Figure 18. DSC for the BiAgX™ mixed solder paste system.

Bond shear strength of the joints, made of the mixed solder paste system and the high lead-containing solder, were compared.

Bond shear tests were performed on TiNiAu-plated Si die on the bare Cu package to simulate typical industry applications. Figure 19 shows the results of the bond strength tests of the joints made using eight different solder pastes (BiAgX with different fluxes) and the high lead-containing solder paste, as reflowed, and also after aging at 200°C for 500 hours. After aging, most of the BiAgX™ pastes did not show obvious softening and the bond strength is relatively higher than the high lead-containing solder. [9]

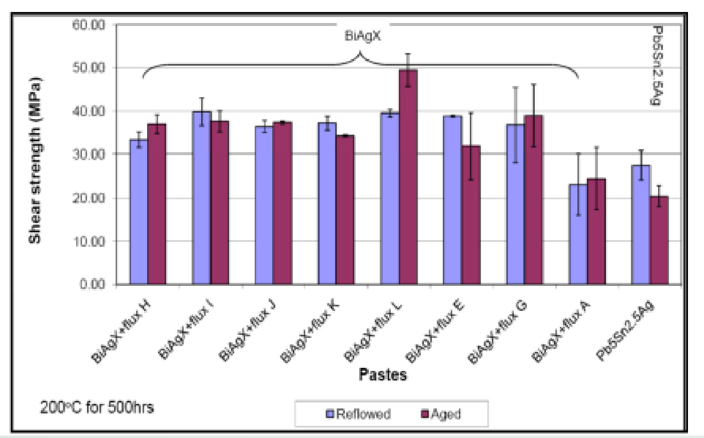


Figure 19. Bond shear strength of the joints after reflow and aged.

Figure 20 shows the bond shear strength measurements after subjecting the samples to thermal cycling at -55°C to +125°C for 2000 cycles. These tests were performed on 0.125” Si die package vehicles. All the different mixes of BiAgX™ solder paste showed a drop on bond strength after the TCT test, but significantly higher strength compared to high lead-containing solder. [9]

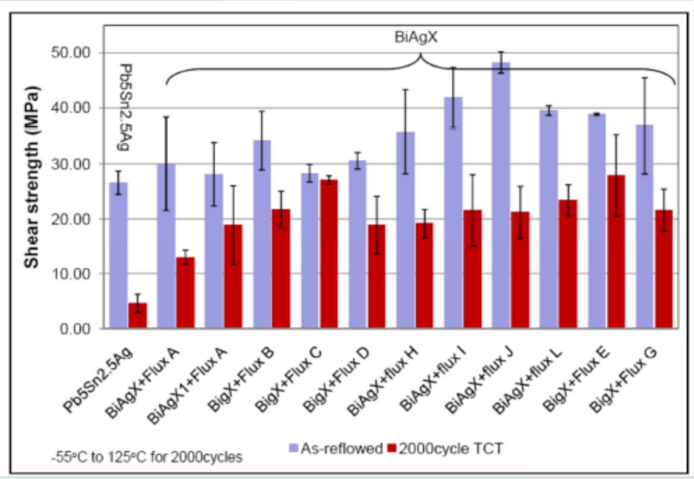
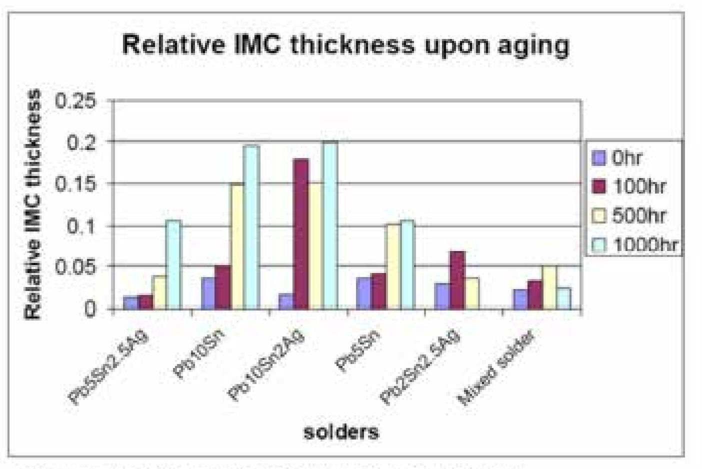


Figure 20. Bond shear strength of the joints after 2000cycles TCT tests.

The IMC layer thickness for the BiAgX™ paste was studied. With increased aging time, the IMC layer thickness (observed through cross-section images) for high lead-containing solders increases, while that of the BiAgX™ solder has no significant change, as shown in Figure 21. The IMC thickness is expressed as the ratio between the measured IMC thickness and the bondline thickness. The insensitiveness of the IMC layer thickness in BiAgX™ is attributable to the fact that most of the reactive element was consumed to form the IMC layer during soldering and no more of the reactive element was available in the joint for further IMC growth towards aging. [9]



* Relative IMC thickness=IMC thickness/Bondinethickness

Figure 21. Relative IMC thickness of high lead-containing solders and the mixed powder solder BiAgX.

Conclusion

In the last several years, the electronics industry has gained substantial experience with Pb-free solders. Some of the limitations of SAC305 are now better understood and continuous work is being done to overcome these limitations. Some of the key challenges of SAC305 were high processing temperature, price volatility of silver, and poor drop test performance. It is understood that a one-alloy solution to address all these challenges is far from sight. The low temperature SnBiAg alloy is suitable for specific applications where the assembly requires low thermal processing to avoid thermal damage on components. The low cost, no-silver alloy Sn992 is available for those who manufacture low-level reliability products. The low Ag SAC with dopant, SACM™ is a promising material for both drop shock and thermal performance, as well as reducing price volatility associated with high Ag content, even though the melting temperature is on the higher side compared to SAC305.

As the package manufacturers who use high-Pb alloys struggle to meet the deadline for RoHS, the potential replacements are being evaluated. BiAgX™ seems to be one of the front runner candidates to meet the deadline. The BiAgX™ solder paste system has shown improvement of bond strength results over the current high Pb-containing alloys.

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