

LOW TEMPERATURE SOLDERING USING SN-BI ALLOYS

Morgana Ribas, Ph.D., Anil Kumar, Divya Kosuri, Raghu R. Rangaraju, Pritha Choudhury, Ph.D.,
Suresh Telu, Ph.D., Siuli Sarkar, Ph.D.

Alpha Assembly Solutions, Alpha Assembly Solutions India R&D Centre
Bangalore, KA, India
siuli.sarkar@alphaassembly.com

ABSTRACT

Low temperature solder alloys are preferred for the assembly of temperature-sensitive components and substrates. The alloys in this category are required to reflow between 170 and 200°C soldering temperatures. Lower soldering temperatures result in lower thermal stresses and defects, such as warping during assembly, and permit use of lower cost substrates. Sn-Bi alloys have lower melting temperatures, but some of its performance drawbacks can be seen as deterrent for its use in electronics devices. Here we show that non-eutectic Sn-Bi alloys can be used to improve these properties and further align them with the electronics industry specific needs. The physical properties and drop shock performance of various alloys are evaluated, and their results are analysed in terms of the alloy composition, including Bi content and alloying additions.

Key words: lead-free, Sn-Bi solders, low temperature soldering, drop shock.

INTRODUCTION

The combined technical and economic benefits of low temperature soldering are expected to grow the use of low temperature solder pastes from <1% to 20% in the next ten years, according to the 2015 iNEMI roadmap [1]. Despite such opportunity for growth, there are limited low temperature alloy options that fulfil SMT soldering requirements. Sn-In and Sn-Bi systems would be obvious options due to their lower melting temperatures, but Sn-Bi lower cost and higher availability puts it at a competitive advantage. Since starting the transition to Pb-free solder, the electronics industry has considered Sn-58Bi as a possible replacement for eutectic Sn-Pb. However, due to its lower ductility and poor thermo-mechanical properties, Sn-58Bi was put aside and used only in limited applications that did not require much of thermal cycling or drop shock performance.

More recently, multi-step assembly processes, a surge in use of temperature sensitive components and industry desire of using cheaper substrates brought in additional challenges and low temperature solders came back under consideration. Furthermore, the miniaturization of portable electronics has also imposed requirements of increasingly thinner flip chip ball grid arrays (FCBGA). Recent investigations have showed that assembling these ultra-thin packages with standard lead-free solders, such as Sn-3Ag-0.5Cu (221°C liquidus temperature), results in dynamic warpage on

package substrate and PCB [2-4]. This represents a severe limitation on using the latest generation of ultra-thin microprocessors. Use of low temperature solders can significantly reduce such warpage, but available Sn-Bi solders do not match Sn-Ag-Cu drop shock performance [5-6]. Besides these pressing technical requirements, finding a low temperature solder alloy that can replace alloys such as Sn-3Ag-0.5Cu solder can result in considerable hard dollar savings from reduced energy cost and noteworthy reduction in carbon emissions [7].

In previous works [8-11] we have showed how the use of micro-additives in eutectic Sn-Bi alloys results in significant improvement of its thermo-mechanical properties. Here we show how a non-eutectic Sn-Bi solder with 2 wt.% additives (referred here as X46) enables peak reflow temperatures as low as 190°C of mixed low temperature/Sn-Ag-Cu solder joints, resulting in significant fewer defects during reflow processing of electronic assemblies.

EXPERIMENTAL DESCRIPTION

Physical Properties

Differential Scanning Calorimetry (DSC) technique was used for assessing the melting characteristics of solder alloys. The experiments were performed using a Differential Scanning Calorimeter from TA Instruments. Samples with 10 mg in mass were heated under nitrogen atmosphere at 10 K/min heating rate. A Running Integral Analysis was performed on all DSC plots to determine the solid/liquid fraction at given temperatures.

Mechanical properties of the alloys were evaluated by tensile tests and elastic modulus measurements. The tensile tests were conducted in a universal testing machine such as the one showed in Figure 1(a). Ultimate tensile strength (UTS) and yield strength (YS), corresponding respectively to the maximum stress achieved during the test and the transition between elastic and plastic deformation, were evaluated as illustrated in Figure 1(b). Each alloy was machined into rounded specimens as per ASTM E8 tensile test standard, with 4 mm diameter and 16 mm gauge length, as showed in Figure 1(c). Stress-strain curves for at least five specimens of each alloy were recorded at room temperature, using a constant strain rate of 10⁻³mm/s. Average values of ultimate strength, yield strength and elongation are reported.

Elastic properties were measured using the ultrasonic pulse-echo technique. We use an ultrasonic thickness gage, and longitudinal and shear wave transducers to measure the sound velocities through the alloys, which are then used to compute their Young's (i.e., elastic modulus) modulus. Through this technique the elastic modulus can be evaluated without the variability often observed when performing tensile tests. The elastic modulus is often used as an insight on the shock and vibration performance of alloys as it is a measure of the stiffness of the material.

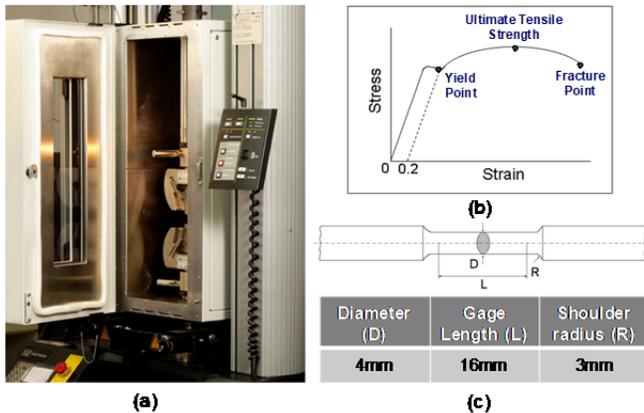


Figure 1. (a) Intron universal testing machine with environmental chamber, (b) Stress-strain curve schematics and (c) Specimen geometry used for tensile testing.

Drop Shock

The ability of solder joints to withstand shock and vibration was evaluated using a board level drop shock test. We use the guidelines described in the JESD22-B111 (July 2003) standard and perform the test following service condition B (1500Gs, 0.5 msec duration and half-sine pulse) for setting up the shock intensity applied during the test. We use a Lansmont shock machine and data acquisition system for test vehicle evaluation and for monitoring the shock pulse curve, Figure 2. The data acquisition system enables detection of specific event conditions for each channel that can be used, for example, for configuring minimum event duration and corresponding voltage levels to detect intermittent electrical and permanent faults. An external power source (5V DC) is applied across the circuit and the generated acceleration is used as a trigger for the measurement of drop in potential gradient across the circuit. We use a test vehicle, showed in Figure 2(b), with 15 CTBGA84 that were assembled and tested till failure. Each failure is accounted once there is a drop of 1V or more in the applied potential, for a duration of 0.5 msec or more. The characteristic life calculated from Weibull plots is given as the number of drops at 63.2% of cumulative failures.

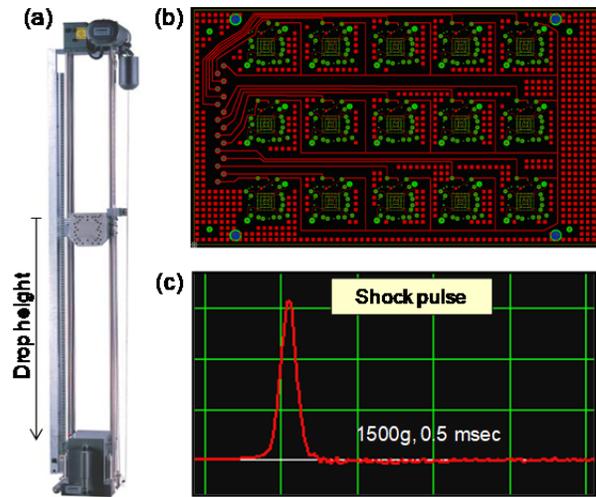


Figure 2. (a) Lansmont drop shock testing machine, (b) Alent drop shock test vehicle and (c) half-sine shock pulse curve corresponding to JEDEC service condition B.

RESULTS AND DISCUSSION

As per their binary phase diagram [12], Sn and Bi form a eutectic composition around 138°C, with about 57 wt.% Bi and 43 wt.%Sn. As Bi content decreases, the liquidus temperature moves away from this eutectic composition, as showed in Table 1. Despite the fact that actual solder alloys have minor impurities, the solidus and liquidus temperatures showed agree well with the phase diagram. When used for SMT applications, the corresponding solder paste is generally reflowed at peak temperatures that are 25-30°C above the solder melting point. Thus, a Sn-Bi alloy with 35 wt.% Bi would need a reflow profile reaching around 211°C, whereas decreasing the Bi content to 40 wt.% would require a peak reflow temperature around 200°C. Such temperatures would be higher than the desirable peak reflow temperature that leads to reduction in warpage and significant cost savings, as discussed earlier.

In the case the Sn-Bi solder is used to assemble an area array package with a higher melting point solder, it is also important to evaluate its transformation into liquid phase. Later we will describe the inter-diffusion between Sn-3Ag-0.5Cu and Sn-Bi, in which these two alloys are joined at temperatures below the Sn-3Ag-0.5Cu melting point. Having the lower melting point alloy in liquid state facilitates the inter-diffusion between these two alloys for forming a solder joint. Table 1 also shows the liquid fraction of Sn-Bi alloys with varying Bi content. As per DSC analysis, when reducing the Bi content to 55 wt.%, the alloy is completely transformed into a liquid phase by 144°C. Further reduction of Bi decreases the fraction of solder that is converted into liquid. For example, reducing Bi content from 50 to 45 wt.% results in a significant decrease in the liquid fraction, from 96% to only 78%.

Since early discussions on the possibility of adopting Sn-Bi alloy as a Pb-free solder, it was clear that their poor mechanical properties, notably excessive brittleness and

lower elongation, would be a deterrent. Figure 3 shows the tensile properties of Sn-Bi alloys with decreasing Bi content. Reducing the Bi content in these alloys does not decrease much the ultimate tensile strength (UTS), but it does improve their elongation, as it was showed earlier [9,13]. Despite such encouraging results, reducing Bi content alone is not sufficient for improving its mechanical reliability in solder joints. For example, Figure 4 shows the effect of room temperature ageing on the Sn-45Bi microstructure. The Bi microstructure (white areas showed in Figure 4) visibly coarsened after only 24 hrs ageing. Hardness measurements confirmed this and showed that Sn-Bi tend to harden upon ageing, in this case increasing from 6.6 to 8.5 Hv2.5 after 24 hrs at room temperature. In addition to that, reducing Bi content alone does not improve drop shock performance to the same level of Sn-3Ag-0.5Cu, as showed in Figure 5. Reducing Bi content from 58 to 45 wt.% increases the drop shock characteristic life in 42%. Further reduction of Bi content to 40 wt.% results in another 77% increase in its drop shock characteristic life. However, despite such improvements in performance by reducing Bi content alone, the drop shock characteristic life of Sn-3Ag-0.5Cu is still 60% higher than of Sn-40Bi, for example.

Another option for improving Sn-Bi alloys mechanical properties is the use of alloying additions. As we showed earlier, alloying additions can be used to improve eutectic Sn-Bi performance such as mechanical properties, drop shock and thermal cycling [8-11]. Table 2 shows the effect of additives such as Ag and In on the melting behaviour of Sn-Bi alloys. Ag addition of up to 1 wt.% does not have a significant change in solidus and liquidus temperature of the alloy. Addition of 1 wt.% In slightly reduces the solidus and liquidus temperature of Sn-58Bi. However, at 3 wt.% In the solidus temperature is reduced to 125°C and the DSC curve showed a peak around 100°C, which indicates presence of lower melting temperature compounds. Other ductile solder alloys can also have appropriate melting behaviour despite having multiple alloying additions. For example, alloy X46 has a solidus and liquidus temperatures of 138°C and 151°C, respectively, and 99% conversion to liquid phase at 144°C (Figure 6).

Table 1. Melting temperatures of various alloys.

Alloy	Temperature, °C		Liquid Fraction, %			
	Solidus	Liquidus	139°C	140°C	142°C	144°C
Sn-55Bi	138	144	10	39	96	100
Sn-50Bi	138	155	6	26	90	96
Sn-45Bi	138	168	9	50	75	78
Sn-40Bi	138	178	16	66	75	77
Sn-35Bi	138	186	12	61	70	77

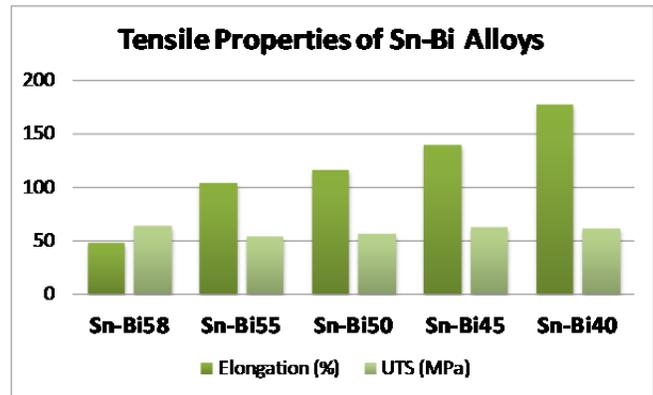


Figure 3. Tensile properties of Sn-Bi alloys. ©2013 IEEE. Reprinted, with permission, from Ref. [9].

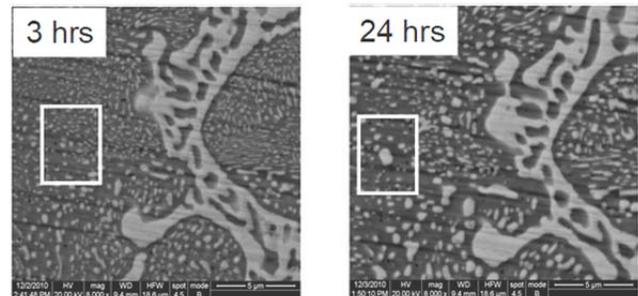


Figure 4. : Effect of aging on the Sn-45Bi microstructure.

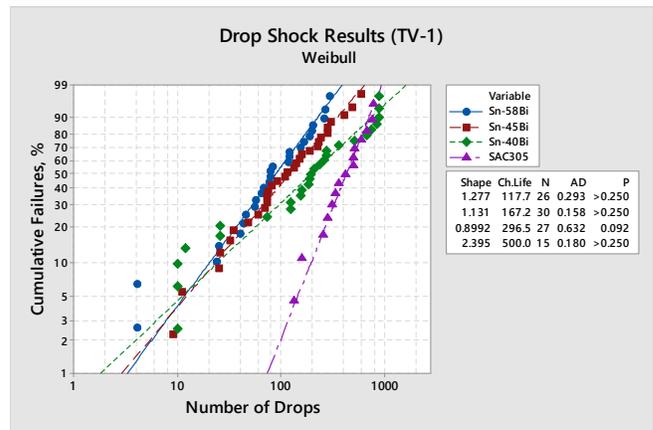


Figure 5. Drop shock results of Sn-Bi alloys.

Table 2. Effect of additives on Sn-Bi solder alloys melting temperature.

Alloy	Solidus Temperature, °C	Liquidus Temperature, °C
Sn-57.6Bi-0.4Ag	137	142
Sn-58Bi-1Ag	137	142
Sn-38Bi-1Ag	137	176
Sn-58Bi-1Ag-1In	133	137
Sn-58Bi-1Ag-3In	125	133*

*Peak at 100°C.

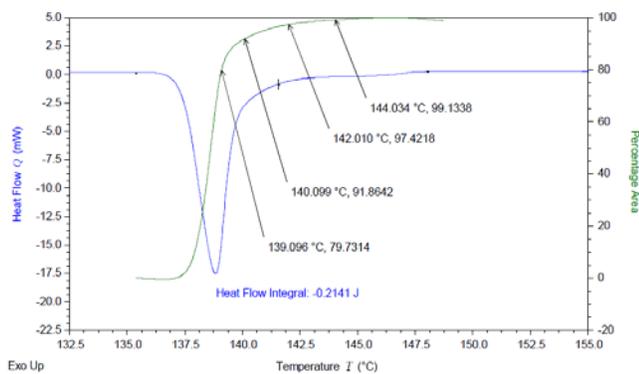


Figure 6. Liquid fractions of X46 alloy computed from DSC curve.

Despite its limited effect on Sn-58Bi melting behaviour, Ag addition can positively impact its mechanical properties. Table 3 shows the effect of these additives on the tensile properties (UTS, yield strength, elongation and elastic modulus). Increasing the Ag addition from 0.4 to 1 wt.% results in higher strength, but somehow lower elongation. Additional 1 wt.% In on the same alloy has minimal effect on its mechanical properties, whereas 3 wt.% In significantly decreases the alloy elongation and elastic modulus. Reducing the Bi content to 38 wt.% and keeping the 1 wt.% Ag addition result in higher UTS and elastic modulus, but lower elongation. X46, which is a non-eutectic alloy with multiple additives has lower UTS than Sn-58Bi-1Ag, much lower yield strength, and higher elongation and elastic modulus.

Before proceeding further, it is important to characterize the mixed Sn-Bi/Sn-3Ag-0.5Cu solder joint. Figures 7 to 10 show examples of such mixed solder joints in which Sn-3Ag-0.5Cu BGAs were assembled using a low temperature solder paste, in this case using X46 alloy. Figure 7 shows an assembly reflowed using a 90-100s soak (100-120°C), 60-90s time above liquidus and 180°C peak reflow temperature. Figures 8 and 9 show assemblies reflowed under similar profile, but with 190°C and 200°C peak reflow temperatures, respectively. Although all three assemblies were reflowed at temperatures below Sn-3Ag-0.5Cu solidus temperature, there is a clear bond between the lower and higher melting temperature solders. Higher magnification images of the Sn-Bi/Sn-3Ag-0.5Cu interface show a zone in which these two alloys inter-diffuse and bond in Figures 7 and 8. Based on these visual observations, the inter-diffusion zone is larger when reflowed at 190°C. Another way to confirm this findings is by measuring the % Bi mixing into the Sn-3Ag-0.5Cu, as showed by Mokler and co-workers [6]. Measurements of the joint height (H_{jh}), joint upper left height (H_{ul}), joint upper right height (H_{ur}) and joint height at the middle (H_{mid}) are used into the following equation: $Bi (\%) = 100 * [H_{ij} - (0.25 H_{ul} + 0.25 H_{ur} + 0.5 H_{mid})] / H_{jh}$. For this particular package, pad and stencil designs, we found that there is 35.8% and 43.2% Bi mixing when the assemblies are reflowed at 180 and 190°C, respectively. Figure 9 shows the complete mixture between these two alloys. The corresponding solder joint heights are

compared side by side in Figure 10, emphasizing their collapse at 200°C.

We started this discussion from the melting behaviour of Sn-Bi alloys, looked into the effect of Bi content on the mechanical properties of solders and investigated the effect of alloying additions to improve these properties. Finally, we use X46 alloy as a proof of concept as to what can be achieved when a balanced alloy composition is used. Earlier we showed that Sn-58Bi drop shock characteristic life is 4.3 times lower than Sn-3Ag-0.5Cu, and that by reducing Bi content this difference was reduced to 1.7 times. Figure 11 shows the drop shock performance of X46 solder alloy versus Sn-3Ag-0.5Cu and Sn-57.6Bi-0.4Ag. We use CTBGA84 components with Sn-3Ag-0.5Cu solder balls, so it forms a mixed solder joint when combined with a solder paste containing the low temperature solder. We observed a dramatic increase in the drop shock characteristic life when we move the solder composition from the near eutectic with minor Ag addition Sn-57.6Bi-0.4Ag alloy to the non-eutectic with 2% additives X46 solder. Indeed, X46 performance (951 drops characteristic life) is equal or better than Sn-3Ag-0.5Cu (875 drops).

Figure 12 shows the drop shock performance of X46 solder using two packages, BGA84 and LGA84. In this way, the performance of the low temperature solder per se can also be evaluated as only X46 solder paste is used to assemble the LGA component. For the mixed X46/Sn-3Ag-0.5Cu solder joints, Sn-3Ag-0.5Cu drop shock characteristic life is 18% higher than X46. In the LGA, the drop shock characteristic life of the unmixed X46 solder joints, achieve identical performance of Sn-3Ag-0.5Cu. As variations from 10 to 20% are expected and considered acceptable within this testing methodology, we can conclude that X46 solder achieves between 82 and 100% of Sn-3Ag-0.5Cu drop shock performance.

Table 3. Effect of additives on tensile properties of Sn-Bi solders.

Alloys	UTS (MPa)	YS (MPa)	Elgtn. (%)	E (GPa)
Sn-57.6Bi-0.4Ag	67.4	58.3	52.6	39.3
Sn-58Bi-1Ag	75.8	68.1	31	39.2
Sn-58Bi-1Ag-1In	78.5	67.7	30.7	38.8
Sn-58Bi-1Ag-3In	74.8	59.2	17.3	37.3
Sn-38Bi-1Ag	82.3	68.5	29.2	42.9
X46	62.2	37.5	40.8	41.4

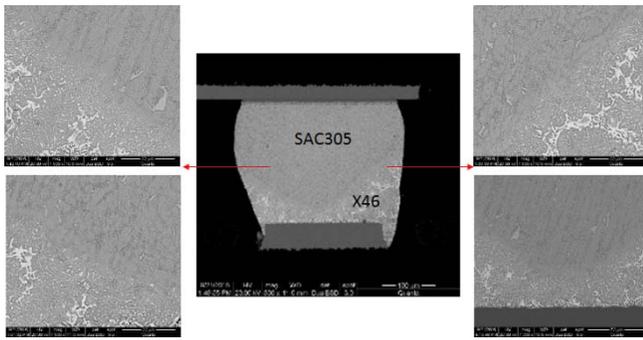


Figure 7. Cross-section of Sn-3Ag-0.5Cu ball and X46 solder paste assembled at 180°C.

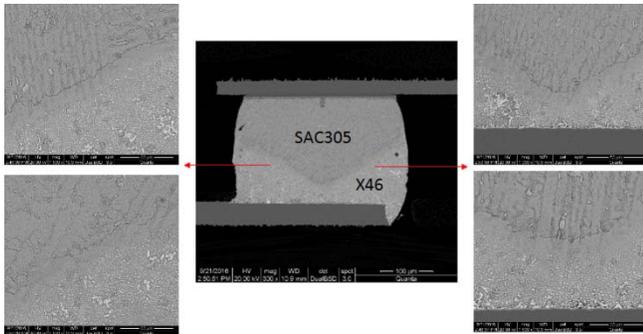


Figure 8. Cross-section of Sn-3Ag-0.5Cu ball and X46 solder paste assembled at 190°C.

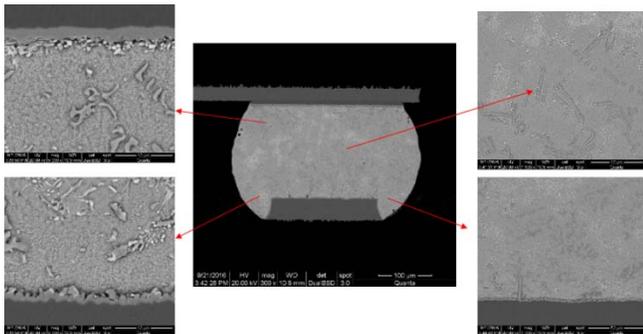


Figure 9. Cross-section of Sn-3Ag-0.5Cu ball and X46 solder paste assembled at 200°C.

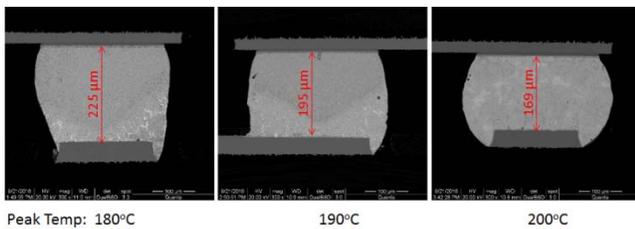


Figure 10. Solder joint height at different peak reflow temperatures.

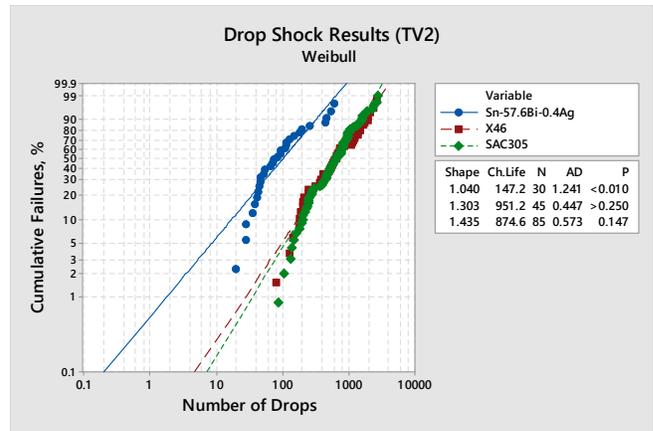


Figure 11. Drop shock performance of X46 alloy using paste flux A.

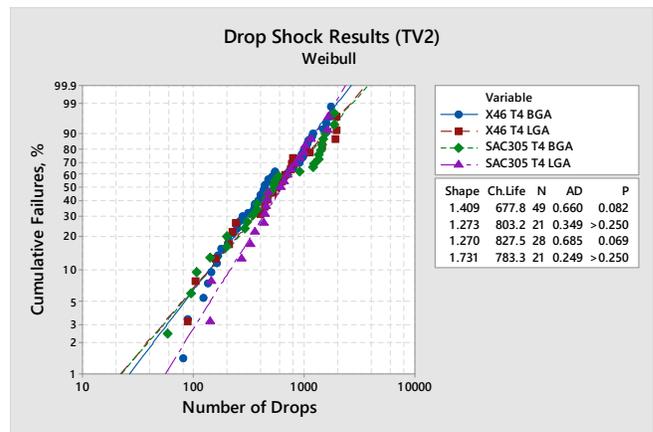


Figure 12. Drop shock performance of X46 alloy using paste flux B.

CONCLUSIONS

In this work we reviewed our latest research on Sn-Bi solder alloys, in which our main observations and conclusions are:

- Bi content should be equal or higher than 40 wt.% for enabling reflow profiles with peak temperature lower than 200°C.
- Reduction of Bi alone does not bring the resulting solders drop shock performance close enough to Sn-Ag-Cu solder.
- Mechanical strength can be improved with Ag addition (up to 1 wt.%), but elongation will be reduced, whereas it is not affected by 1 wt.% In addition. However, 3 wt.% In results in a brittle solder that starts melting as early as 100°C.
- X46 and Sn-3Ag-0.5Cu solders inter-diffuse at 190°C reflow temperature, forming a mixed solder joint that has between 82 and 100% of Sn-3Ag-0.5Cu drop shock performance, for CTBGA84.
- Unmixed solder joints of non-eutectic Sn-Bi+2% additives X46 solder match 100% of Sn-3Ag-0.5Cu drop shock performance, for LGA84.

Finally, a balanced alloy composition is key for achieving the desired performance results. As such, solder alloy

compositions and properties have to be carefully evaluated. The results showed here for X46 solder clearly demonstrate that Sn-Bi alloys can be used in applications that require Sn-3Ag-0.5Cu mechanical sock reliability, depending on their alloy composition.

ACKNOWLEDGEMENTS

We thank the Applications and Chemistry Labs at the India R&D Centre for their key support to this work. We are also grateful to other colleagues that eventually have participated in the discussion of the work from which this manuscript is derived.

REFERENCES

- [1] iNEMI roadmap, 2016.
- [2] Aspandiar, R. et al., "Investigation of Low Temperature Solders to Reduce Reflow Temperature, Improve SMT Yields and Realize Energy Savings". Proceedings of the 2015 APEX Conference, February 2015.
- [3] Chen, O. H. et al., "Comparison of the Mechanical Shock/Drop Reliability of Flip Chip BGA (FCBGA) Solder Joints Formed by Soldering with Low Temperature BiSn-Based Resin Reinforced Solder Pastes". Proceedings of the International Conference on Soldering and Reliability, 2015.
- [4] Chen, O. H. et al., "Soldering SAC Solder Balls BGAs with BiSnAg and Resin Reinforced BiSn-Based Solder Pastes". Proceedings of SMTA International, September 2015.
- [5] Chen, O. H. et al., "Mechanical Shock and Drop Reliability Evaluation of the BGA Solder Joint Stack-Ups Formed by Reflow Soldering SAC Solder Balls BGAs with BiSnAg and Resin Reinforced BiSn-Based Solder Pastes". Proceedings of SMTA International, September 2015, Rosemont-USA, pp.215-222.
- [6] Mokler, S. et al., "The Application of Bi-based Solders for Low Temperature Reflow to Reduce Cost while Improving SMT Yields in Client Computing Systems". Proceedings of SMTA International, September 2016, Rosemont-USA, pp.318-326.
- [7] News.lenovo.com. (2017). Lenovo™ Announces Breakthrough, Innovative PC Manufacturing Process | Lenovo Newsroom. [online] Available at: <http://news.lenovo.com/news-releases/lenovo-announces-breakthrough-innovative-pc-manufacturing-process.htm> [Accessed 29 Jun. 2017].
- [8] Ribas, M. et al., "Low Temperature Alloy Development for Electronics Assembly". IPC APEX, San Diego – USA, February 2013.
- [9] Ribas, M. et al., "Development of Low-Temperature Drop Shock Resistant Solder Alloys for Handheld Devices". Proceedings of IEEE 15th Electronics Packaging Technology Conference, Singapore, December 2013, pp.53-57.
- [10] Ribas, M. et al., "Thermal and Mechanical Reliability of Low-Temperature Solder Alloys for Handheld Devices". Proceedings of IEEE 16th Electronics Packaging Technology Conference (EPTC), Singapore, December 2014, pp.366-371.

[11] Ribas, M. et al., "Comprehensive Report on Low Temperature Solder Alloys for Portable Electronics". Proceedings of SMTA International, September 2015, Rosemont-USA, pp.176-183.

[12] Baker, H., ASM Handbook, Alloy Phase Diagrams (1992). Materials Park, Ohio: ASM International.

[13] Takao, H. et al., "Mechanical Properties and Solder Joint Reliability of Low-Melting Sn-Bi-Cu Lead Free Solder Alloy". R&D Review of Toyota CRDL, Vol. 39, No. 2 (2004), pp. 49-56.