High Reliability Mid-Temperature Pb-Free Alloy for Multi-Step Soldering

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Abstract 166

High silver Sn-Ag-Cu solder alloys, such as Sn-3Ag-0.5Cu (SAC305), result in solder joints with high mechanical and thermal reliability, and can sustain relatively high operational temperatures. However, their melting point (generally above 217ºC) requires at least 240-250ºC reflow temperatures, putting additional stresses on printed circuit boards. Solder alloys allowing for lower reflow temperatures can be very advantageous, adding benefits such as long-term reliability, lower energy cost and reduced cycle time and enabling multi-step soldering. Here we present our new Pb-free solder alloy that allows for a 25-30ºC reduction in peak reflow temperatures. We investigate the effect of various alloying additions into the mechanical properties of three alloys, 1N, 3D and 3E. We also investigate the thermal cycling performance of these alloys when used as solder paste. The results presented here show that solder alloy 3D enables peak reflow temperatures as low as 215ºC, in combination with higher mechanical properties and improved fatigue life that is significantly higher than SAC305.

Introduction

Restrictions in using Pb in soldering materials due to its toxic nature have propelled the widespread use of Pb-free soldering materials [1-4]. Besides, its unique combination of electrical, chemical, physical, thermal and mechanical properties, eutectic Sn-Pb solders with relatively lower melting point (183ºC) had a series of advantages [4]. Besides the savings in energy, perhaps the most significant were that lower reflow temperatures enabled using cheaper substrates and components [5-7]. Indeed, there was a massive effort from the whole industry to find assembly materials compatible with the new Pb-free soldering scenario, in which peak reflow temperatures of at least 240-250ºC were required [8, 9].

Nowadays the use of lead-free soldering materials has become widespread, either due to environmental directives or pressure from the end users [1-4]. However, due to electronics miniaturization and novel designs, the range of requirements for Pb-free alloys is also changing [9]. Among these, reducing reflow temperatures has been quite a challenge for the soldering materials industry, despite the significant benefits involved. In certain applications involving temperature sensitive components, it is desirable to use soldering alloys having melting temperature of 200ºC or lower. As solders, these alloys also need to fulfill standard requirements for electronics packaging and assembly, such as good solderability, high joint strength and high reliability [1-4].

Therefore, such alloys would allow multi-step soldering, i.e., multiple reflows of the same printed circuit boards (PCB) in which various components are assembled using multiple reflow profiles. In this way, very critical components could still be assembled with regular Pb-free solders such as Sn-3Ag-0.5Cu, whereas other critical components would be assembled in a subsequent reflow using a low temperature solder. Examples of applications for such alloys are LED light engines, general lighting and consumer applications.

In this work, we have investigated the effect of In, Ag and Bi additions in the Sn-Ag-Cu alloy system. In order to achieve high resistance to thermal fatigue, solder alloys are required to have high temperature creep resistance, which can be attained by combining solid solution strengthening and precipitation/ dispersion hardening to improve the mechanical strength of metallic Sn [10]. Elements with higher solid solubility in Sn are Bi, Cd, In and Sb. All four of them can contribute, in various degrees, towards solid solution strengthening of the Sn matrix, but we do not use Cd, due to its high toxicity, and Sb, due to possible environmental restrictions and high melting point. Various alloy compositions were short-listed on the basis of their liquidus temperature and mechanical properties. Among these, three alloys (1N, 3D and 3E) were selected for further testing, especially due to their lower liquidus temperatures and narrow melting range. Here we present the melting behavior, mechanical properties and thermal cycling performance of these new mid temperature alloys.

Experimental Procedure

Alloys were cast using a liquid metallurgy route, at temperatures between 270 and 280ºC. The compositional analysis was done by ICP-OES, and the alloys were tested for hardness, toughness and tensile strength. Toughness was evaluated using a standard Charpy impact test method (ASTM E23-16b). Tensile tests were performed at room temperature at 10^{-3} mm/s displacement, as per ASTM E8 standard test method.

The short-listed alloys were processed into type 4 powders and mixed into a paste using an appropriate paste flux for further reliability evaluation. As per IPC J-STD-006A standard, a type 4 powder refers to less than 0.5% particles < 50 µm, maximum 10% between 38-50 µm, minimum 80% between 20-38 µm, maximum 10% < 20 µm. The proportion between powder and paste flux was such that we obtained 88.5% metal loading. The PCBs were assembled using the reflow profile as shown in

Figure 1. Soaking was done at 130-170°C for 120 seconds. The time above liquidus (TAL), 200°C, was 80 seconds, while the reflow peak temperature was 215°C.

Thermal fatigue tests were carried out in an Espec thermal cycling chamber (air-air) TSA-101S, where the samples cycled from -40 to +125°C, with 10 minutes dwell time at each temperature. The tests were carried out for a total of 2,000 cycles, with samples also being taken out at regular intervals for analysis. For thermal reliability tests, Alpha Cu-OSP drop shock test vehicle with CTBGA84 components was used for in-situ monitoring of electrical resistivity of the components followed by measurement of IMC thickness and failure analysis. These ball grid array (BGA) components have a 7 x 7 mm body size and 0.5 mm pitch and 0.3 mm diameter Sn-3Ag-0.5Cu spheres. Increase of electrical resistance values to 20% or more of the initial value for five consecutive readings was considered a failure as per IPC 9701-A [11].

Shear boards, showed in Figure 2(b), were used to study the effect of thermal cycling on the shear strength of the chip resistor joints. Chip shear tests were conducted on a DAGE 4000 system, which is capable of performing chip shear tests using 100 kg load cartridges. The chip shear test was carried out according to JIS Z3198-7:2003 [12] standard. For these tests, test parameters were maintained at the test speed of 700 µm/s, and shear height of 20 µm and 50 kg test load throughout the test. Both the test vehicles used here are shown in Figure 2. The BGAs and chip resistor solder joints, before and after thermal reliability tests, have been examined using a scanning electron microscope (SEM) from FEI (model Quanta 400). All the measurements of microstructure were done using the SCANDIUM Image Analysis software.

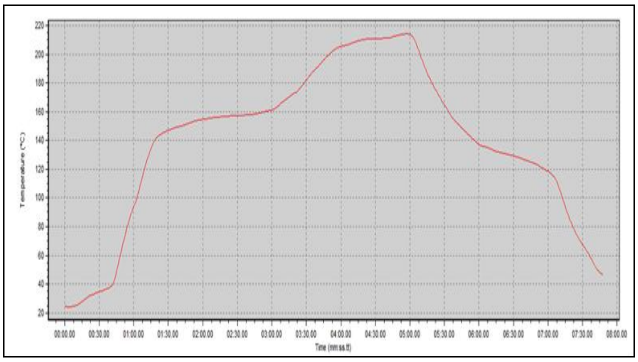
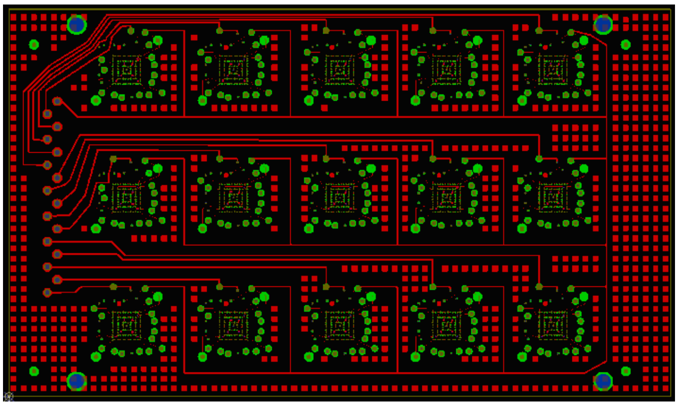
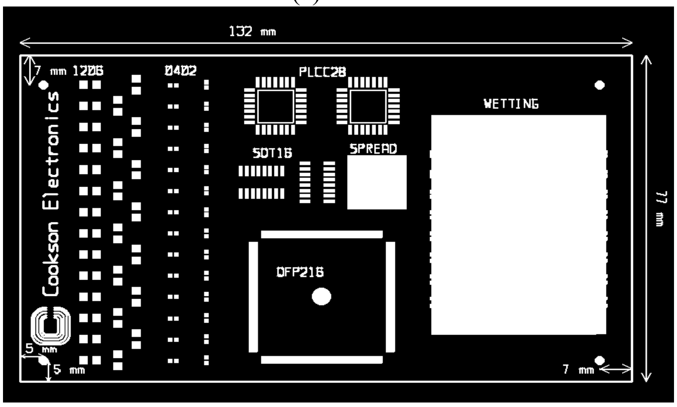


Fig. 1. Reflow profile



(a)



(b)

Fig. 2. (a) Drop shock and (b) Shear board used in thermal cycling test

Results and Discussion

Bulk Alloy Properties

We substantially decreased solidus and liquidus temperatures of all the alloys, as shown in Table 1. However, the new alloys have significantly high hardness as compared to SAC305 which has resulted in a decrease in their toughness values (Figure 3).

Table 1. Melting behavior of selected alloys

Alloys	**Melting Range (°C)**
SAC305	217 - 220
1N	195.3 - 207.6
3D	191.9 - 203.2
3E	186.8 - 199.5

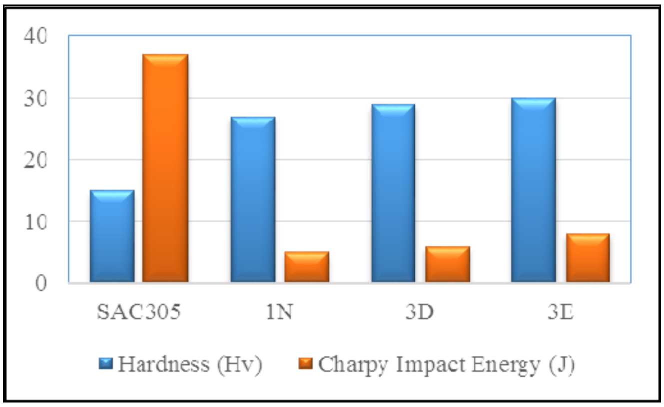


Fig. 3. Hardness and toughness of the alloys.

Figure 4 shows a significant increase in tensile strength of these alloys (more than double), when compared to SAC305. Figures 5 and 6 show the effect of the two major strengthening elements on the toughness and tensile strength. Increasing Bi reduces toughness, whereas, more than 6 wt.% addition of In has remarkable effect on toughness (Figure 5). Increasing In has a significant effect on yield strength too, but negligible effect on ultimate tensile strength (UTS), as shown in Figure 6. Thus, moderate Bi and high In give the best strength properties.

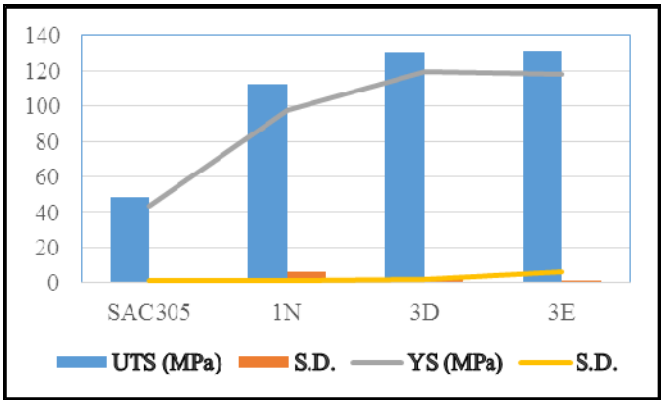


Fig. 4. Tensile strength of bulk alloys

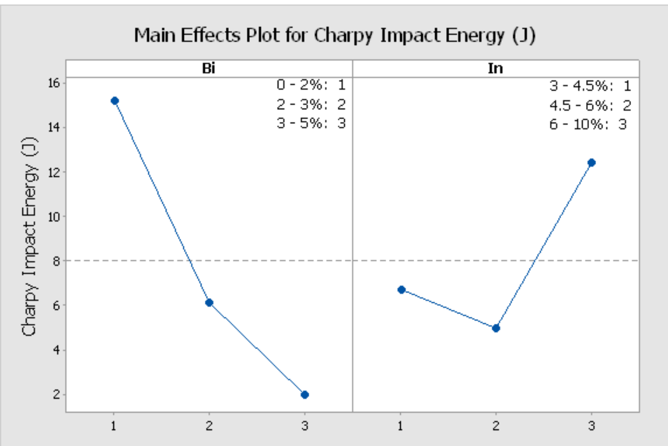


Fig. 5. Effect of Bi and In on alloy toughness

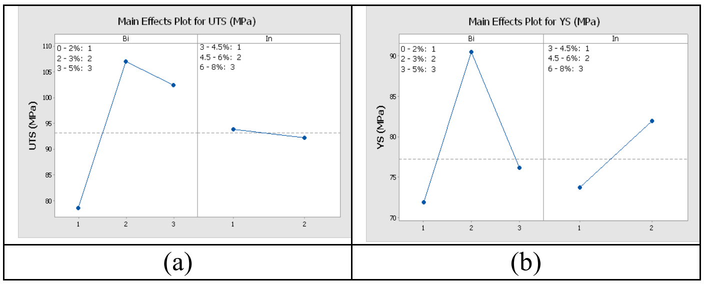


Fig. 6. Effect of alloying elements on (a) ultimate tensile strength and (b) yield strength

Owing to miniaturization of solder joints in modern electronic devices, traditional tensile testing is incapable of predicting the mechanical behavior of real solder joints in electronic packages [9]. Decreasing size of electronic components makes the interconnections more susceptible to mechanical failure. This is because mechanical stresses generated in solder joints when assemblies expand or contract with temperature changes, increase with decreasing size of interconnections. Therefore, reliability of solder joints is an important factor in the design of electronic devices [13].

The results of the accelerated thermal cycling test are shown in Table 2. The absence of electrical failures in any of the new alloys shows that the joints remain strong and reliable under thermal cycling conditions. The BGA joints were cross-sectioned after thermal cycling to understand the microstructure evolution and find the failure mode (Figure 7). Ag_3Sn intermetallics (IMC) were observed in all the alloys. In general, the cracks initiate and propagate through the bulk near the IMC/ solder interface. The much higher hardness of the IMC causes a stress concentration to be produced at the IMC/ solder interface during thermal cycling [9]. Cracks were not observed before 1500 thermal cycles owing to their very strong and reliable joints.

Table 2. Thermal cycling results

Alloys	**Cumulative Failures, %**			
	500 cycles	**1000 cycles**	**1500 cycles**	**2000 cycles**
SAC305	0	0	2.2	4.4
1N	0	0	0	0
3D	0	0	0	0
3E	0	0	0	0

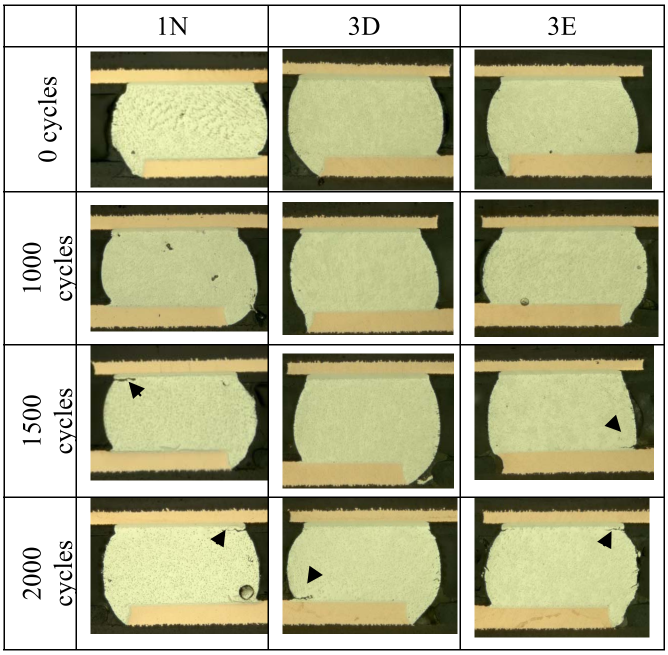


Fig. 7. Effect of thermal cycling on CTBGA84

The reported shear results represent an average 20 measurements of 1206 chip resistors, and are shown in Figure 8 (a). Alloy 1N undergoes minimum (18%) loss in shear strength in chip joints. Alloy 3E has shown very large loss in joint strength after thermal cycling, and was, subsequently, discarded. The IMC thickness, as measured on the PCB side of the BGA cross-sections, is similar for all the new alloys after 2000 cycles of thermal cycling as observed in Figure 8(b). The IMC in all the new alloys grew to a maximum of 4 µm which is well within the range of acceptance for most electronic applications.

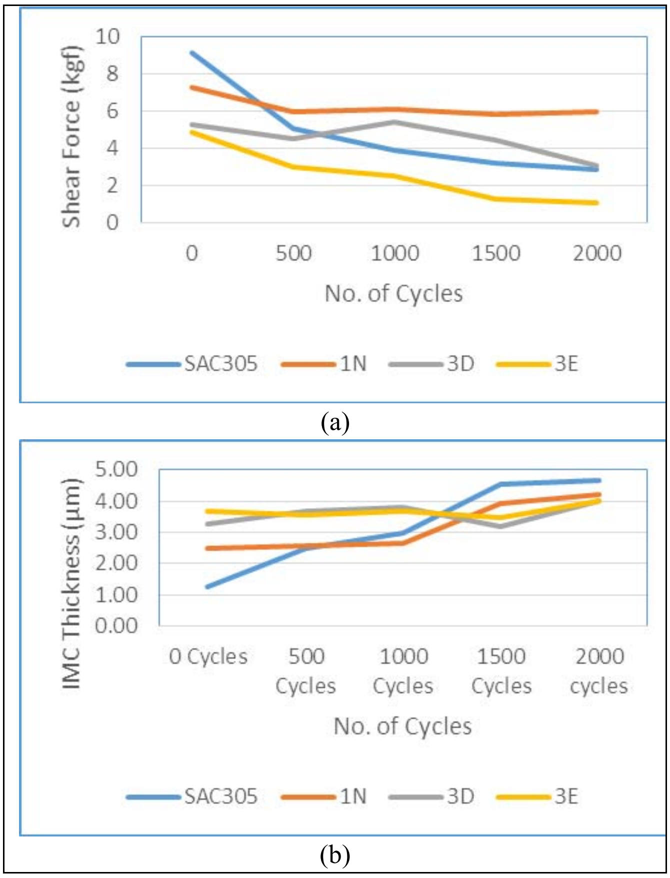


Fig. 8. Effect of thermal cycling on (a) joint strength and (b) IMC thickness

Conclusions

High reliability Pb-free solder alloys having melting point below or around 200°C are strongly desired by the electronics industry for energy and materials savings and to enable multi-step soldering of the same PCB. We showed here the resulting evaluation of three mid-temperature solder alloys and concluded that:

- The reflow peak temperature has been reduced significantly by 25-35°C, when compared to standard solder pastes using Sn-3Ag-0.5Cu.
- Elemental additions have contributed to IMC formation and strength retention at high operational temperatures.
- Besides lower melting temperatures, both alloys 1N and 3D have superior mechanical and thermal reliability properties.

Considering its lower liquidus temperature and excellent thermal cycling performance, alloy 3D is recommended for applications that require ultra-high reliability performance at lower reflow temperatures. Examples of such applications include, but are not limited to, LED light engines, general lighting and consumer applications.

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References

[1] Liu N. S. and Lin K. L. , "Microstructure and mechanical properties of low Ga content Sn-8.55Zn-0.5Ag-0.1Al-xGa solders", *Scripta Materialia,* vol. 52, (2005), pp. 369-374.
[2] Liu N. S. and Lin K. L., "The effect of Ga content on the wetting reaction and interfacial morphology formed between Sn-8.55Zn-0.5Ag-0.1Al-xGa solders and Cu", *Scripta Materialia,* vol. 54, (2006), pp. 219-224.
[3] Shen J. et al., "Effects of minor Cu and Zn additions on the thermal, microstructure and tensile properties of Sn-Bi-based solder alloys", *J. Alloys and Compounds*, vol. 614, (2014), pp. 63-70.
[4] Abtew M. and Selvaduray G., "Lead-free Solders in Microelectronics', *Materials Science Engg. R,* vol. 27 (2000), pp. 95-141.
[5] Ronnie Teo J. W. and Sun Y. F., "Spalling behavior of interfacial intermetallic compounds in Pb-free solder

joints subjected to temperature cycling loading", *Acta Materialia*, vol. 56 (2008), pp. 242-249.
[6] Tsao L. C. et al., "Effects of nano – Al_2O_3 additions on microstructure development and hardness of Sn3.5Ag0.5Cu solder", *Materials and Design,* vol. 31 (2010), pp. 4831-4835.
[7] Lee J. G. et al., "Residual-mechanical behavior of thermodynamically fatigued Sn-Ag based solder joints", *J. Electronic Materials*, vol. 31 (2002), pp. 946-952.
[8] Babaghorbani P., Nai S. M. L. and Gupta M., "Reinforcements at nanometer length scale and the electrical resistivity of lead-free solders', *J. Alloys and Compounds,* vol. 478 (2009), pp. 458-461.
[9] Zimprich P. et al., "Mechanical size effects in miniaturized lead-free solder joints", *J. Electronic Mater*ials, vol. 37 (2008), pp. 102-109.
[10] Choudhury P. et al., "New lead-free alloy for high reliability, high operating temperature conditions", *ICSR (Soldering and Reliability) Conference Proceedings,* Rosemont, IL., September (2014).
[11] 'Performance test methods and qualification requirements for surface mount solder attachments', IPC-9701A, IL, USA, 2006.
[12] 'Test methods for lead-free solders – Part 7: Methods for shear strength of solder joints on chip components', JIS Z 3198-7, JIS, Tokyo, Japan, 2003.
[13] Loomans M. E. et al., "Investigation of multi-component lead-free solders", *J. of Electronic Mater*ials, 23 (1994), 741-746.