

EFFECT OF Bi CONTENT ON PROPERTIES OF LOW SILVER SAC SOLDERS

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ABSTRACT

Since the adoption of RoHS and REACH regulations for electronics manufacturers, Sn-Ag-Cu (SAC) alloy systems have largely replaced the Sn-Pb solder alloys with Sn-3Ag-0.5Cu (wt%) (SAC305) the most widely accepted. This high silver content SAC alloy (greater than X percent) has a major deficiency however, the relative fragility of the solder joint. This is due to the formation of primary Ag_3Sn platelets crystals in the solidified structure leading to poor drop-shock performance causing major concerns for portable devices. Lowering or eliminating Ag content of SAC has been proposed as a solution but with limited success. In this work, a systematic study is presented to address the effect of Bi content on soldering and mechanical performance of low silver SAC alloys. Thermal behavior (melting and solidification), wetting and spreading performance, and tensile and hardness properties of alloys are compared and a promising lead-free SAC-Bi solder alloy that also demonstrates tin whisker mitigation properties is recommended.

Key words: Lead-free solder, electronic assembly, wettability, mechanical properties, melting, tin whisker

INTRODUCTION

Soldering is the most important part of assembly process of electronic components. Among many various criteria for creating a robust solder joint are wettability, spreading, thermal behavior (melting and solidification), mechanical properties such as tensile strength and creep resistance, thermal and electrical conductivity and cost. Prior to RoHS, Sn-Pb alloys had been widely used as the main solder material for electronic packaging due to its low cost, relatively low melting temperature, superior wetting behavior, high reliability and relatively good mechanical performance. However, due to environmental and health concerns from the toxicity of lead (Pb), it has been banned for use in electronic and electrical devices, resulting in extensive study to find a suitable replacement. Fig. 1 illustrates how rapidly the global solder industry responded to the demand for lead-free solders in many electronic applications. Among the lead-free alternatives, Sn-Ag-Cu (SAC) alloys are regarded as the de facto replacement for Sn-Pb solders. The most popular of these alloys is SAC305

containing 3% silver, 0.5% copper and the balance (96.5%) tin (wt.%).

The relatively high silver content of SAC305 introduces two major concerns related to performance and cost. SAC305 is prone to drop-shock and creep failure due to the formation of large Ag_3Sn platelets and poor creep resistance [6,7]. SAC alloys exhibit high undercooling that is associated with the difficulty of nucleating Sn solidification as a pro-eutectic phase. Thus, during slow cooling, e.g., in ball grid array (BGA) joints where cooling rates are slow ($<0.2^\circ C/s$), the high undercooling of the joints can promote formation of undesirable pro-eutectic intermetallic phases, particularly Ag_3Sn blade-like phase, that tend to coarsen drastically making the as-solidified solder joints more brittle [6]. In addition, the price of silver has increased drastically over the last several years driving the industry for lower silver or lower cost solder alloys.

The aim of this study is to examine a low silver content alloy to reduce the solder cost and improve mechanical performance by elimination of primary large Ag_3Sn platelets. However, by lowering Ag content of SAC alloy, melting temperature will increase. The addition of bismuth (Bi) as a low cost element can reduce the melting temperature and improve mechanical properties. Bi may also reduce mitigate tin whisker growth which is very important in the context of lead-free solders in high reliability electronic assembly. Thus, in this work binary Sn-0.7Cu is taken as the base solder alloy. The presence of copper (Cu) reduces the copper dissolution rate from the terminal pad. The silver (Ag) content of the alloy is kept below 1% and the added Bi from low (0.5%) to high (22%) values. Soldering and mechanical performance of the alloys are studied and compared.

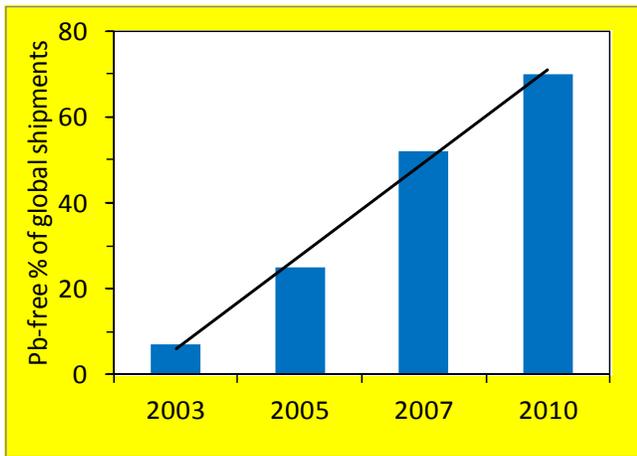


Figure 1. Global consumption of lead-free versus tin/lead solders (in wt%). In 2010, for example, worldwide consumption of lead free solder was at 70%, whereas it was 30% for tin/lead [5].

EXPERIMENTAL

Twelve alloys with varying Bi content (Table 1) were prepared in an electric pot with graphite crucible. The composition of solder alloys was analyzed by arc emission spectroscopy. The molten alloys were cast into round ‘dog-bone’ shape in a stainless steel mold for tensile testing. The tensile specimens with the dimensions shown (Fig.2) were annealed at 125°C for 96 hr. to remove any residual stress or inhomogeneity induced during the sample preparation. Tensile tests were performed at room temperature with a constant strain rate of 10^{-3} s^{-1} . For each alloy at least five specimens were tested to ensure reproducibility of the tensile test results. Hardness of all the specimens was also measured by Vickers micro-hardness testing machine with 10gf load and 10s impression time.

Table 1. Compositions of solder alloys (wt%)

Sn	Cu	Ag	Bi
Bal.	0.7	0.6	0-22

Thermal behavior of the alloys was investigated with differential scanning calorimetry (DSC). A piece of 50-100mg alloy was heated in an aluminum cell at heating rate of 10°C/min under nitrogen atmosphere followed by cooling to room temperature at -10°C/min cooling rate. Each alloy was tested twice and the reading was based on the second run.

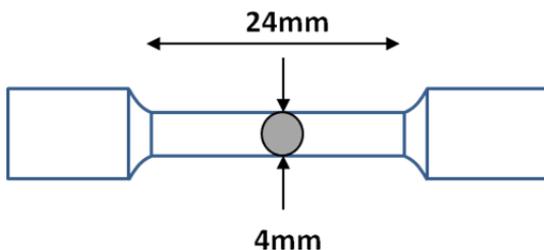


Figure 2. Dimensions of round bar tensile specimen (dog-bone).

Wettability is a critical factor when evaluating the performance of a solder alloy. The wetting process is dynamic during soldering and the solid/liquid interfacial tension between solder and substrate varies as the wetting proceeds. Wettability can be quantified with wetting balance technique that measures wetting force between molten solder and solid substrate versus wetting time. Wettability of the alloys was therefore quantified with wetting balance technique. A copper plate coupon (25mm×6mm×0.5mm) used as the substrate was immersed in a bath of liquid solder alloy and the wetting force was measured over time. The wetting balance curve displays the vertical component of force (F) applied by the wetting balance load cell on copper coupon (see Fig. 3). This technique will provide real-time wetting force that can be evaluated as wetting performance of solders and fluxes. In the typical wetting balance curve shown in Fig. 3b, ‘ t_0 ’ is the time for the wetting curve to recross the buoyancy force line and the contact angle falls to $\Theta = 90^\circ$, this time is called zero cross time. In this study, the time ‘ t_0 ’ and the maximum force are taken as wetting time and wetting force, respectively. An alcohol based no clean flux (AIM NC 265) was used to flux/prepare the substrate surface. Each test was repeated three times and the average value was reported. Details of wetting balance test condition are shown in Table 2.

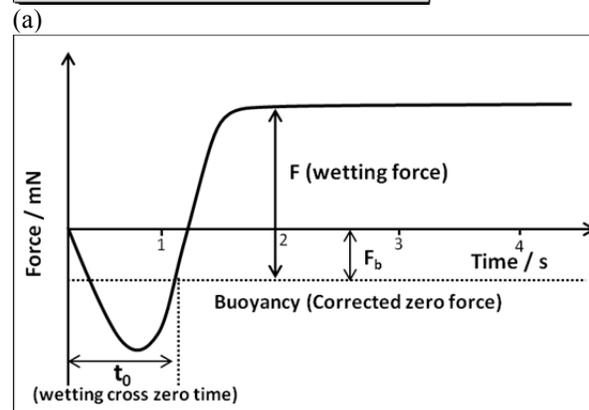
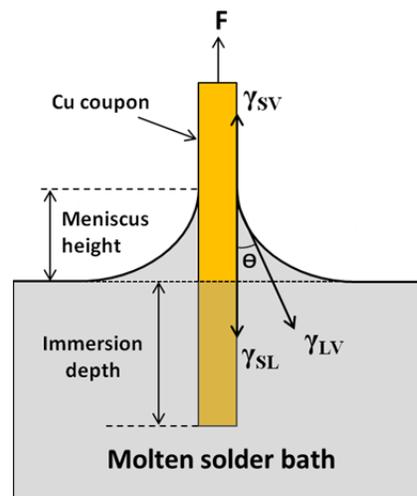


Figure 3. (a) Wetting balance test running on Cu coupon immersed in molten solder bath. Wetting force (F), contact

angle (Θ), surface tensions at the solid-liquid (γ_{SL}), solid-vapor (γ_{SV}) and liquid-vapor (γ_{LV}) interfaces are schematically shown. (b) Typical wetting curve shows the wetting balance force versus wetting time.

Table 2. Wetting balance test parameters

Molten alloy temperature	265°C
Pre-heat time	10 sec
Immersion speed	20 mm/s
Immersion depth	6 mm
Immersion time	5 sec

In order to evaluate tin whisker growth, a 2mm diameter copper wire was fluxed and dipped into the molten solder pot followed with wiping in order to give a uniform coating thickness. The coated wire was then stressed by making a “U-shaped” bend to 90 degrees. These samples were exposed to an accelerated whisker growth condition, i.e. in an environment chamber with 60°C temperature and 85% relative humidity. The surfaces of samples were regularly examined with scanning electron microscope (SEM) for tin whisker growth.

RESULTS AND DISCUSSION

Thermal Behavior

DSC heating curves (heat flow versus temperature) are shown in Fig. 4. The valleys represent intense endothermic phase transitions, i.e. melting. Based on thermal behavior of the alloys DSC diagrams are separated in two plots in Fig. 4: the top diagram for relatively low Bi alloys and bottom diagram for high Bi alloys. DSC results clearly show that high Bi content SAC-Bi alloys that form very low melting temperature phase (circled) and are not suitable for further consideration. Thus, the focus of this work was directed to lower Bi content alloys.

In order to better understand effect of Bi on the thermal behavior of the alloys, a thermodynamic calculation based on Scheil-Gulliver solidification model was carried out using the FactSage™ thermodynamic software [8]. The calculated weight percent of liquid phase in each alloy as a function of temperature is illustrated in Fig. 5. The solidification model which is partial equilibrium approach (full diffusion of solute in liquid but no diffusion in solid) shows that the low melting temperature phase is significant (>15%) in alloys with Bi content of 10% and above. However, the low amount of liquid phase solidified at low temperature (~140°C) in low Bi alloys (Bi<6%) explains the absence of detectable low temperature peak in DSC curves.

For solidus determination of the alloys the temperature of the first visible onset of melting has been taken. In other words, as soon as a deflection from the baseline of DSC curve occurs, melting is taking place. For liquidus the peak temperature is taken. Fig. 6 depicts that the solidus and liquidus of SAC-Bi alloys decrease linearly in parallel

fashion with increasing Bi content up to about 3wt% Bi. However, the solidus and liquidus parallel lines start to deviate at higher Bi content as depicted with dashed line at 3% Bi in Fig. 6. Pasty range which is defined as the difference between solidus and liquidus temperatures (see Fig. 7) increases slightly with Bi content up to 3 %; however, the increase is drastic above 3% as depicted in Fig. 7.

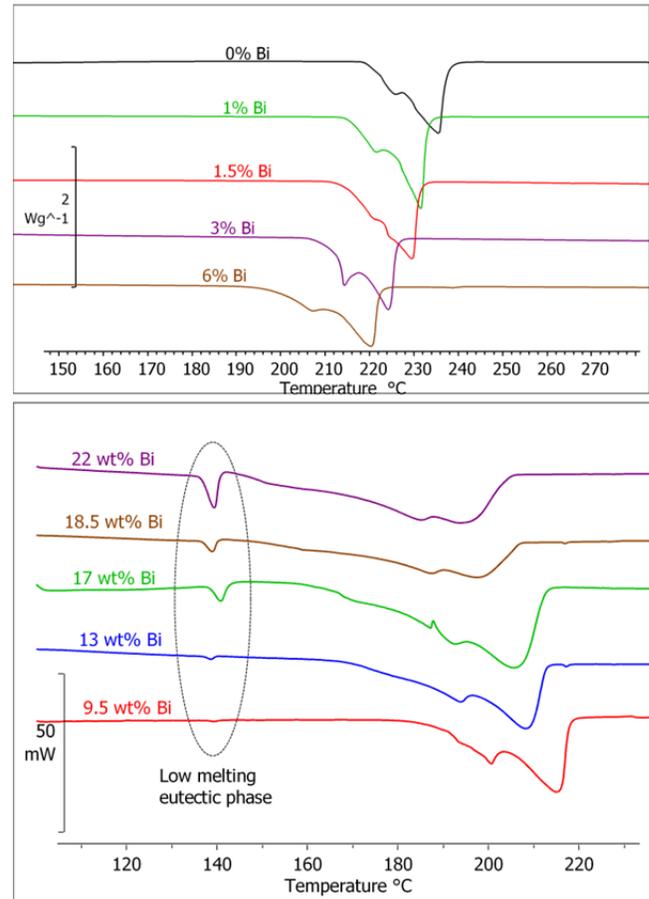


Figure 4. Heating curves (heat flow vs. temperature) of the alloys at the heating rate 10°C/min: top diagram shows low Bi (Bi<6%) content SAC0607-Bi alloys and bottom diagram shows high Bi (>9%) content SAC0607-Bi alloys with low melting phase peak.

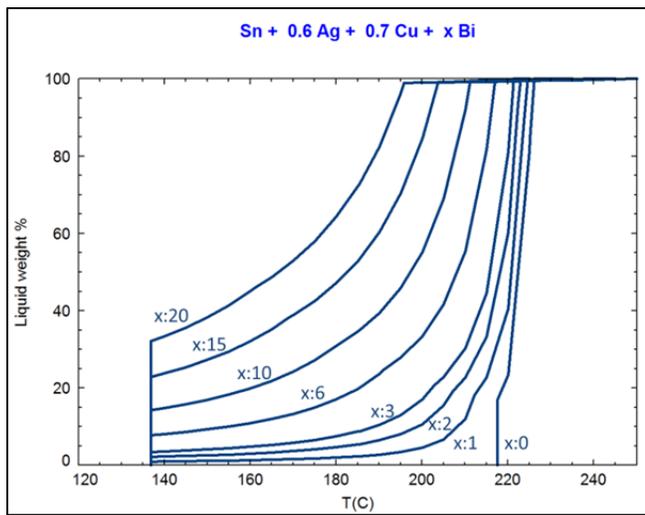


Figure 5. Calculated liquid fraction vs. temperature of SAC-Bi alloys at different Bi contents.

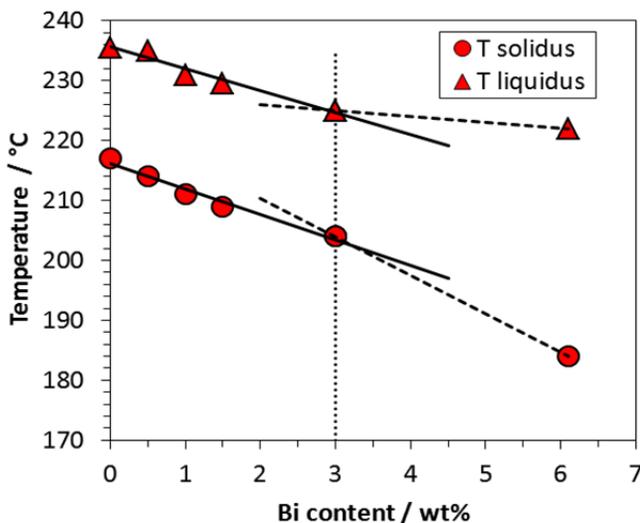


Figure 6. Solidus and liquidus temperatures of the alloys determined by the first deflection of the baseline in DSC curve. Parallel solidus and liquidus lines deviate at 3% Bi.

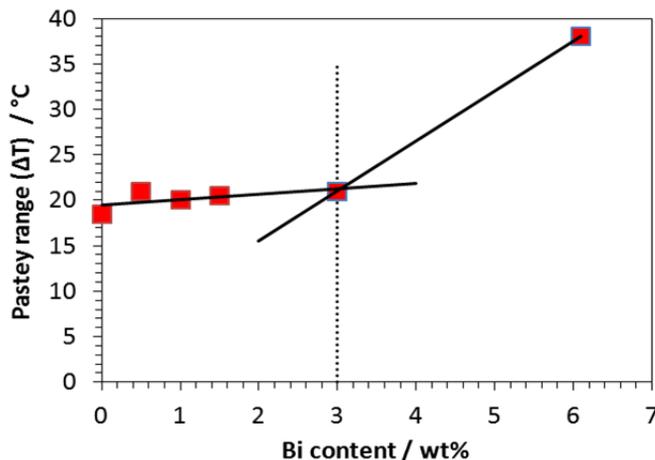


Figure 7. Variation of pasty range of the SAC-Bi alloys with Bi content.

Mechanical Properties

Tensile stress-strain curves of the alloys (Fig. 8) show that by increasing Bi content the strength of SAC-Bi alloys increases while ductility decreases. Bi bearing alloys all show higher strength as compared to that of SAC305. Fig. 9 shows that the increase of tensile strength with Bi content is linear. However, elongation decreases with addition of Bi content in a non-linear fashion and follows a power law function up to 3% Bi as shown in Fig. 10. The elongation of 6% Bi alloy falls below the power law fitting equation indicating a rapid reduction in ductility of the alloy. Furthermore, consistent with tensile strength results, hardness data (Fig. 11) also demonstrates that the hardness of alloys increases linearly with Bi content.

Solid solution of Bi in Sn is the main strengthening mechanism [9]. Precipitation of Bi in β -Sn matrix at higher Bi content may also contribute in strengthening of the alloys. A thermodynamic calculation of equilibrium phases illustrated in Fig. 12 confirms that all Bi dissolves in the matrix at Bi concentrations below 3wt%. Therefore, the only strengthening mechanism is solid solution of Bi in β -Sn. Since Ag and Cu contents are kept constant, concentrations of intermetallic phases, i.e. Ag_3Sn (0.8 wt%) and Cu_6Sn_5 (1.8 wt%) remain identical for all the alloys. The equilibrium calculation also shows that when Bi content is above 3 wt% the concentration of Bi particles increases as a result of limited solubility of Bi in β -Sn. Thus, precipitation hardening mechanism may also contribute in mechanical properties of the alloys.

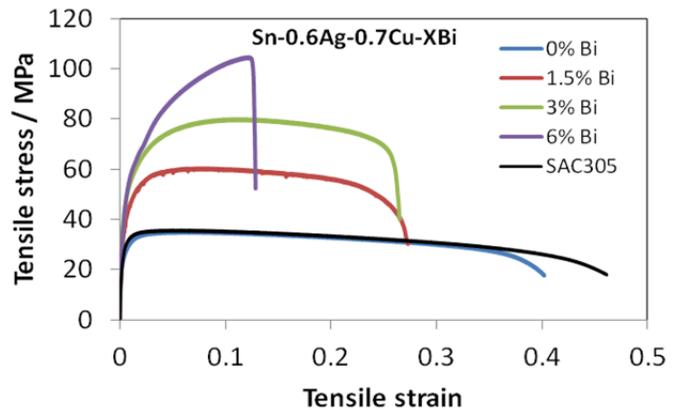


Figure 8. Tensile stress-strain curves of annealed specimens. SAC305 is shown for comparison.

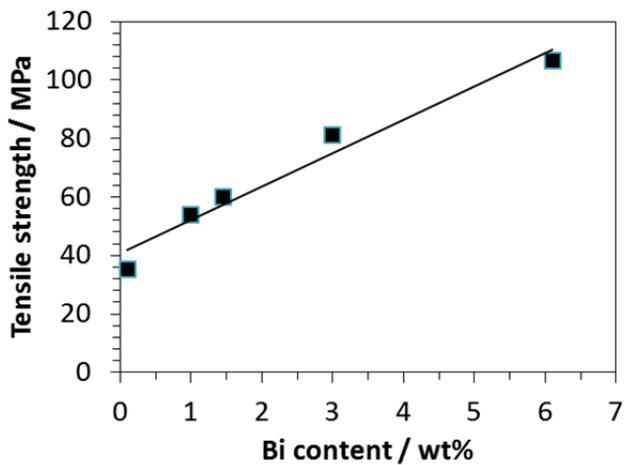


Figure 9. Tensile strength of SAC-Bi alloys changes linearly with Bi content.

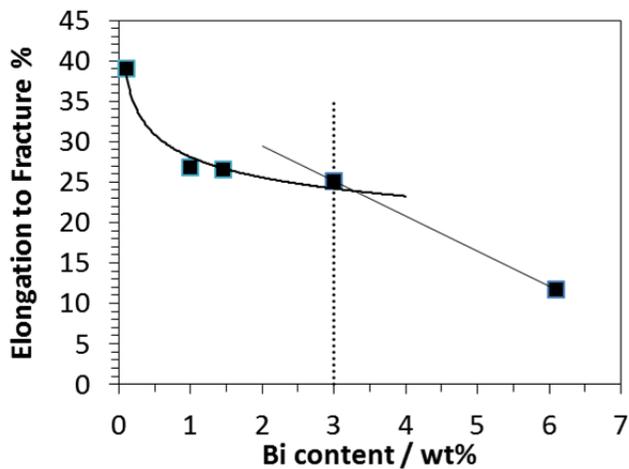


Figure 10. Tensile elongation of the alloys in the annealed condition. Up to 3% Bi the elongation fits with a power law equation. Elongation decreases more rapidly in alloy with higher concentration of Bi (6%).

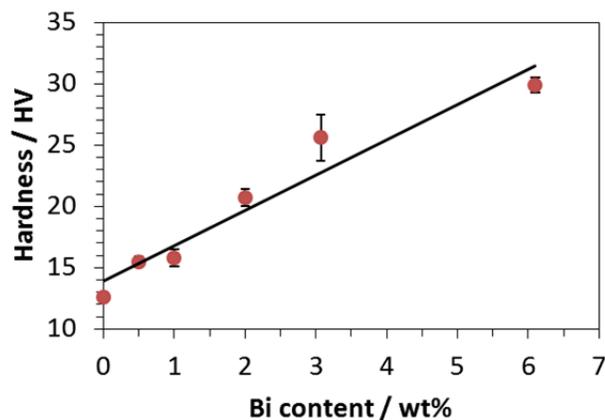


Figure 11. Hardness of the alloys in the annealed condition.

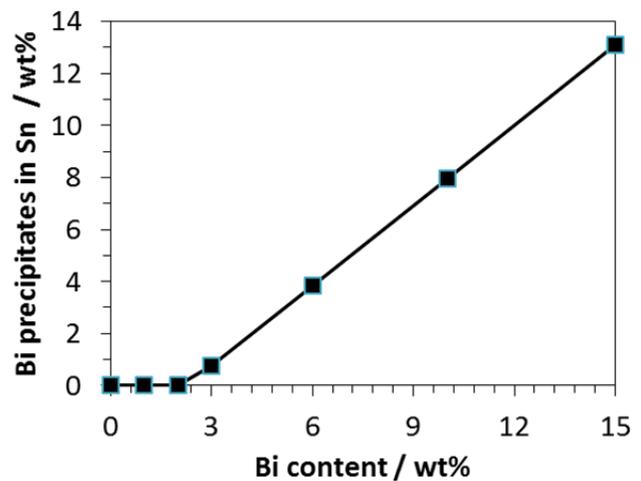


Figure 12. Equilibrium calculated wt% of Bi phase precipitated in β -Sn at 25 °C for the alloys Sn-0.6Ag-0.7Cu-XBi. Other phases calculated for the alloys are: 0.8 wt% Ag_3Sn , 1.8wt% Cu_6Sn_5 with balance of β -Sn.

Wetting Behavior

The wetting balance test results are shown in Fig. 13. It is found that bismuth addition above 2wt% improves wettability of SAC-Bi alloys by increasing wetting force and reducing wetting time as demonstrated with the shifting wetting curve towards top left of SAC0607 curve. Graphs of wetting time (t_0) and wetting force as function of Bi content are shown in Fig.14. Fig.14a clearly shows that Bi addition increases the wetting speed. The trend is captured with a single polynomial function. The fact that addition of Bi reduces the melting temperature of the alloys (see Fig. 6) can explain why wetting time decreases with Bi additions at constant wetting test temperature. Trend for wetting force (Fig.14b) is slightly different. Wetting force increases with addition of Bi up to about 3%. When the Bi content increases further ($Bi > 3\%$) maximum wetting force drops to lower values. In other words, the optimum Bi content to improve wetting force is about 3 wt%. As shown in Fig. 14b the maximum wetting force follows a parabolic diagram with highest wetting force around 3% Bi content.

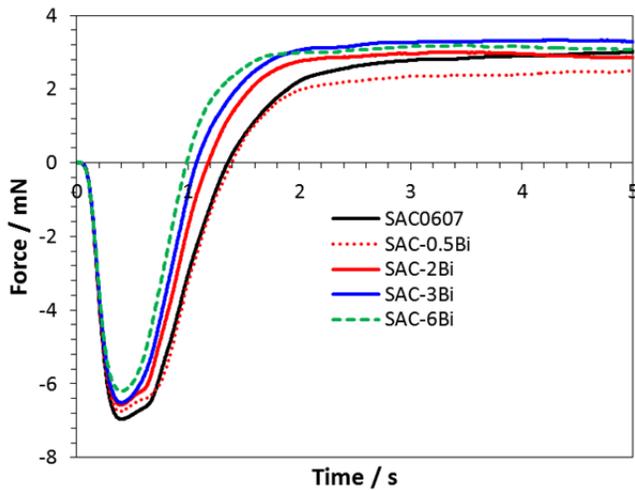


Figure 13. Wetting force balance curves of the alloys at 265°C

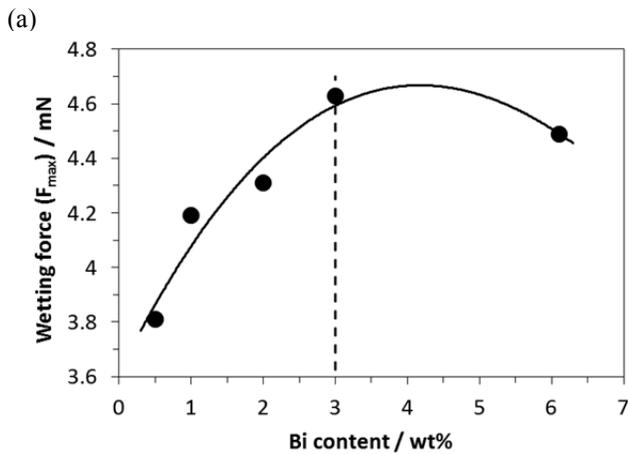
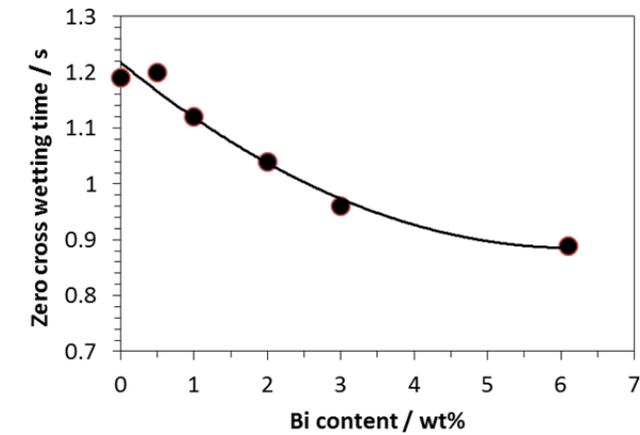


Figure 14. (a) Variation of zero cross wetting time, and (b) maximum wetting force with Bi content. Wetting time (t_0) decreases with addition of Bi content in all concentrations studied, whereas wetting force shows a peak around 3% Bi.

Tin Whisker

For tin whisker evaluation the alloy with optimum properties that is SAC-3Bi was evaluated against reference

SAC305. Fig. 15 shows SEM image of the bend area of wire where observation of whiskers was carried out. Tin whiskers are observed in SAC305 samples soaked in testing chamber for 2600hr and 3100hr (see Fig. 16). However, there is no obvious trace of whiskers on SAC-3Bi sample after 2600hr and 3100hr soaking. Nevertheless, some signs of whiskers nucleation may be realized for SAC-3Bi sample soaked for 3100hr (Fig.16). The results show that whisker growth is effectively suppressed by Bi addition which is consistent with previously published references [10, 11]. Mitigation of tin whisker growth with addition of Bi is attributed refining of grain size structure and also suppressing intermetallic growth at grain boundaries allowing grain boundary migration and releasing compressive stresses. In this work we did not perform detail microstructure study to verify the suggested mechanism for mitigation of tin whisker growth.

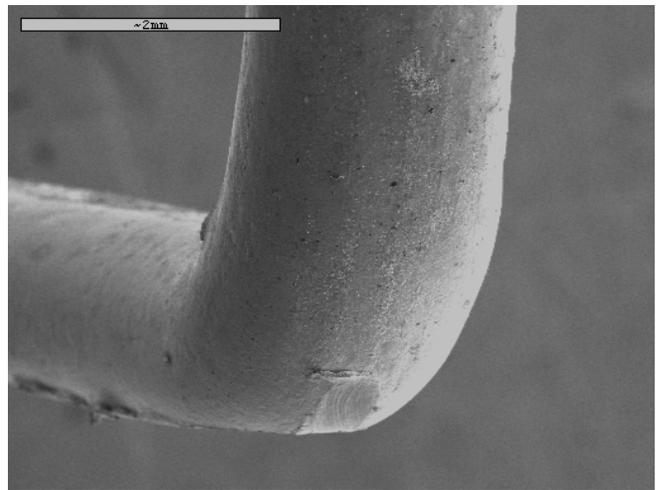
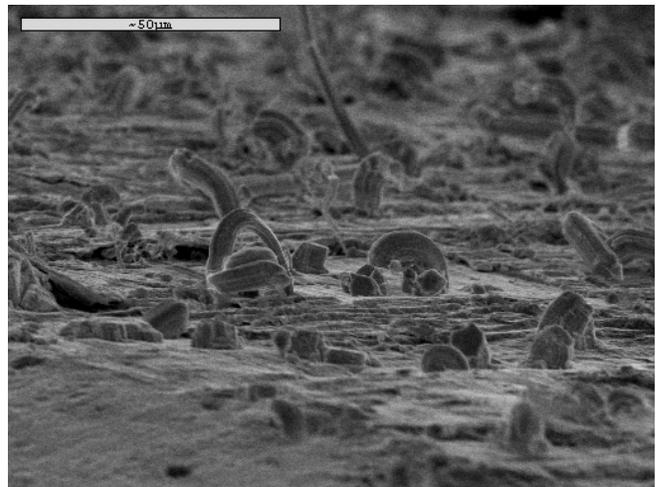
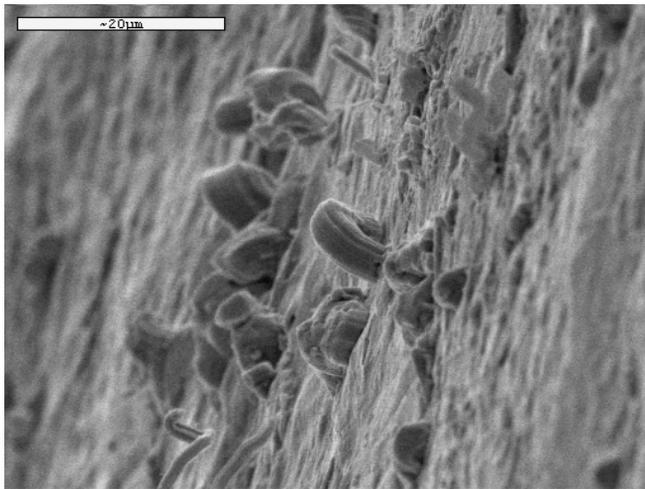


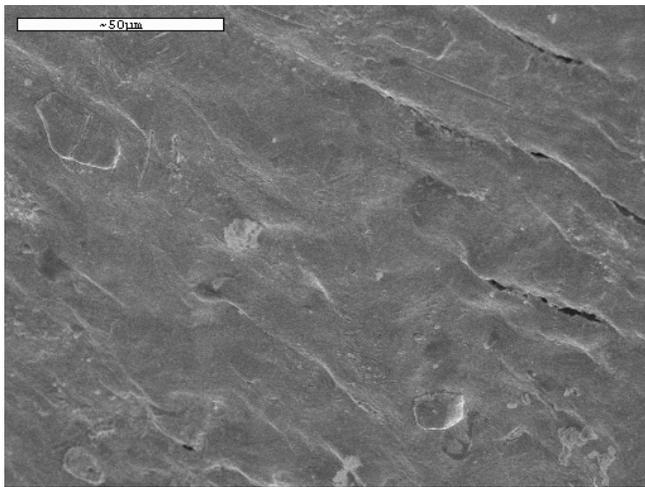
Figure 15. SEM picture showing the bend area of the wire where tin whisker growth is examined.



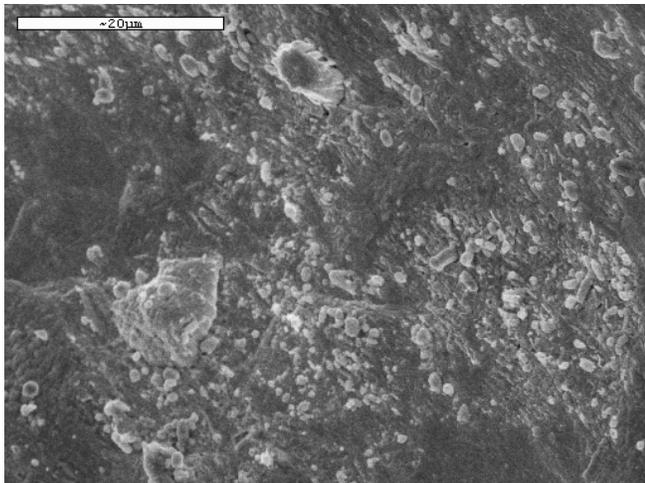
SAC305 (2600hr)



SAC305 (3100hr)



SAC-3Bi (2600hr)



SAC-3Bi (3100hr)

Figure 16. SEM surface evaluation of copper wire coated with SAC305 and SAC-3Bi after 2600 hr. and 3100hr in 60°C and 85% RH chamber.

SUMMARY

A systematic study on low silver SAC0607-Bi solder alloys was carried out in order to propose an alloy with optimum soldering and mechanical properties. Properties such as thermal behavior, wetting performance, hardness and tensile strength, as well as tin whisker growth were investigated and compared with reference SAC305.

The following conclusions can be summarized:

- Alloys with Bi contents higher than 6% form a detectable low melting temperature phase
- Melting temperature of SAC-Bi alloy decreases linearly with increasing Bi content up to 3%.
- Pasty range which the difference between solidus and liquidus temperatures increases drastically with Bi content above 3%.
- Tensile strength and hardness both increase linearly with Bi content in the range of 0-6 wt%.
- Tensile elongation decreases with Bi addition. The trend is more rapid in the alloy with high concentration of Bi, i.e. 6%. This is attributed to additional strengthening mechanism; precipitation hardening that is activated at high Bi contents (Bi>3%).
- Wetting time decreases with Bi additions. Optimum wetting performance (short wetting time and high wetting force) is obtained for the alloy with 3% Bi.
- Tin whisker growth is mitigated in SAC-Bi alloy as compared with SAC305.

Based on the soldering and mechanical data in this study, it is concluded that SAC0607-3Bi is the best choice in terms of melting, wetting, mechanical and reliability performance as compared to SAC305.

Future work will include the manufacturability, process capability and product reliability of SAC0607-3Bi for electronics assembly.

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REFERENCES

- [1] M.M. Schwartz, ASM handbook: vol. 6, Welding, Brazing and Soldering, editors: D.L. Olson, T.A. Siewert, S. Liu, G.R. Edwards, ASM Int.1993, 126-137.
- [2] L. Zhang, C.-W. He, Y.-H Guo, J.-G Han, Y.-W Zhang, X.-Y Wang, Microelectronics Reliability 52 (2012) 559-578.
- [3] G. Zeng, S. Xue, L. Zhang, L. Gao, J Mater Sci : Mater Electron (2011) 22 : 565-578.
- [4] M. Abtey, G. Selvaduray, Mater Sci Eng 27 (2000) 95-141.
- [5] IPC Market Research Services, Global consumption of tin/lead versus lead free solder, www.ipc.org.

- [6] A.J. Boesenberg, I.E. Anderson, J.L. Harringa, J Electron Mater 41 (2012) 1868-181.
- [7] A.Z. Miric, SMTA Int. Conf., Orlando, FL, Oct. 2010.
- [8] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melancon, A.D. Pelton, S. Petersen, CALPHAD 26 (2002) 189-228.
- [9] M. Maalekian, Y. Xu, A. Nobari, K. Seelig, International Conference on Soldering and Reliability, Toronto, 2015.
- [10] N. Jadhav, M. Williams, F. Pei, G. Stafford, E. Chason, J. Electron. Mater. 42, 312 (2013).
- [11] J. Jo, S. Nagao, K. Hamasaki, M. Tsujimoto, T. Sugahara, K. Sukanuma, J. Electron. Mater. 43, 1 (2014).