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Mechanical strength and its variability in Bi-modified Sn-Ag-Cu solder alloy

M. Matahir, L.T. Chin, K.S. Tan, A.O. Olofinjana*
Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Brunei BE1410
* Corresponding author: E-mail address: ayodele.olofinjana@ubd.edu.bn

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Properties

ABSTRACT

Purpose: Many previous work on Sn rich Pb-free soldering had focused on the evolution, morphology and the role of interfacial intermetallic compounds (IMC) layers of Cu_3Sn and Cu_6Sn_5 on the mechanical integrity of soldered joints. However recent studies had shown that under static shearing stress, more fracture failures had been found to occur through the solder and thus indicate the significance of solder microstructures in the joint integrity. In this work, we investigated the effect of Bi substitution for Sn on the shear strength of solder joints of near eutectic SAC alloy Sn3.5Ag0.9Cu.

Design/methodology/approach: Ingot alloy were prepared from pure elements and their melting characteristics were followed with thermal analyses. Copper plates were soldered together in lap joints that were subjected to shear testing in the as-soldered conditions. The microstructures were followed by SEM and EDS.

Findings: Results show that failures occurred in quasi-brittle manner, with large variability. The ternary SAC alloy had average shear strength of 30 MPa better than binary eutectic Sn/Cu. Small Bi substitution of Sn up to 2 wt% lead to increased average shear strengths with maximum strengths of about 50 MPa recorded for compositions with Bi content of 0.5 to 1.5 wt%. Bi substitutions beyond 2wt% gave substantially lower strength values. The application of Weibull criteria suggest untypical high variability in strength with Webuill moduli less than 10. Higher variability in shear strengths were found in compositions containing more than 2 wt.% Bi.

Research limitations/implications: Micro-structural evidence suggest that the role of Bi in increasing strength may be related to the high solubility of Bi in Sn and this would have provided some solution hardening effect. Higher Bi content however, lead to the formation Bi rich phases in the microstructure and this would have affected the mechanics of deformation thus leading to generally lower strength values and much higher variability in measurements.

Originality/value: This paper clarifies the role of Bi substitution in improving the mechanical properties and reliability of soldered joints with unleaded solders.

Keywords: Reliability assessment; Pb-free solders

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1. Introduction

Soldering is an important process in the manufacture of electronic devices where components need to be joined together with sufficient mechanical integrity that would provide reliability in normal operations. The ubiquitous printed circuit board (PCB) in electronic devices rely solely on surface mount technology (SMT) that depends on excellent soldering practices [1-3]. Pb-Sn solders have sufficiently fulfil this role for more than five decades. The most commercially available leaded solders are based on compositions around the eutectic Sn-37Pb with the Sn-40Pb in particular widely used in electronic interconnects [1].

Despite the good soldering properties of Pb-Sn, health concerns remains on the environmental hazard posed by the use of Pb-bearing materials. The European Union (EU) have now passed and are implementing new directives on the Restriction of Hazardous Substances (RoHS) and on the disposal of waste electronic and electrical equipment (WEEE) [4, 5].

RoHS and other global legislative efforts to reduce hazardous materials in electronics placed severe restrictions on the use of leaded soldered alloys in electronic components and thus provide a strong push for the development of lead-free solders. Japanese and European industries are now recommending the use of certain ternary Sn-Ag-Cu (SAC) alloys as lead free solders.

The drive for Pb-free solders development is towards systems that can imitate conventional PbSn alloys in terms of melting temperatures and possibly improved mechanical properties. A candidate Pb-free solder needs to fulfill the following requirements: wettability, low melting temperature, small melting range, good mechanical properties, good resistance to mechanical and thermal fatigue, corrosion resistance, good electrical properties, non-hazardous, easily available and low material cost [6]. A lot of efforts have therefore been devoted to the development of alloys that meet these criteria and many reviews (eg. [1, 7-8]) have been published.

With the existing pressures on miniaturization of electronic devices, the need for strong reliable soldered joints has increased in order to meet the high density packing. The added implication also is that the high current densities accompanying the high density portable electronics raises concern on electromigration damage. The newer Pb free solders are therefore faced with more stringent requirements as dictated by high density packaging [7, 9].

From the many reviews [1, 7-8], Sn rich ternary system with eutectic around Sn3.5(±0.2)Ag0.9(±0.2)Cu are widely accepted as suitable replacements for the leaded solder in electronic interconnects. Though the melting range 217-224°C is substantially higher than the 183°C eutectic temperature in the Pb-Sn system, the higher melting temperature is not considered a serious hindrance to its acceptance. However, the high chemical activity of Sn in Sn rich solders means that the new Pb-free solders are susceptible to the formation of IMC phases either in the as-soldered condition or after aging. Many studies [10-12] had indeed implicated the growth of interfacial IMCs of the types $(Cu,Ni)_3Sn$ and $(CuNi)_6Sn_5$ as the cause for brittle failure and decreased reliability Sn rich solders. The study of the role of IMC either in the solder body or at interfacial joints on strength and reliability is very important. Small additions of other rare earth elements were thought to decrease growth of IMC but the high oxidation tendencies of these can introduce other complications. While the role of interfacial IMC cannot be overemphasized, especially in thermal fatigue, recent studies [13] however, demonstrated that under static shear stress, failures in joints appear across solder body despite the existence of well-established IMC layer. This thus emphasizes the need to study the strengths in soldered joints under such loading. The case for small volume of the solder too is expected to introduce variability in the results. Here we investigated the shear strengths of as-soldered joints using copper lap joints for near eutectic alloys centered around the composition Sn3.5Ag0.9Cu with Bi substitution for Sn.

2. Experiments

2.1. Alloy preparation

40 g ingot of alloys were made by weighing commercially pure elements Sn, Ag, Cu and Bi in proportion of the weights for the target compositions. The mixtures were poured into a preheated alumina crucible containing a molten eutectic salt mixture of LiCl/KCl that is being heated on a propane gas flame. The metal mixture was allowed to melt and the molten salt protects the molten alloy from oxidation. During melting and cooling prior to solidifying, melt was stirred by a glass rod.

2.2. Thermal analysis

The melting characteristics of the sample alloys were studied using the Setaram thermal analyser in the differential scanning calorimetry (DSC) mode. The melting properties of the alloys were determined using a thermal program designed to suit their predicted melting behaviours. For binary alloys, phase diagrams from literatures were used as a guide to their predicted melting behaviours. For higher order alloys, reasonable estimates were made guided by the binary precursor. Typically, a thermal program consists of a rapid heating at a rate of 50°C/min from room temperature to temperature of about 30°C below the expected melting point. This is followed by slower heating rate of 1°C/min over the expected melting range after which it is rapidly cooled at a rate of 40°C/min back to room temperature. For every scan, about 40 to 80 mg sample was loaded into alumina sample pans and Ar was used as the sweeping gas.

2.3. Electron microscopy and EDS

Sections for microstructural analysis were polished to 3 μm finish. Acidic Ferric chloride was use to etch and this etch Sn revealing the IMC distribution. Samples were examine on Tescan SEM with accelerating voltage at 20 kV. Oxford Instrument EDS attached to the SEM was used to confirm microstructural components.

2.4. Shear strength measurement

For shear strength tests, two copper plates were lapped joined together using an alloy solder as the feeder metal over a flame. The joined plates were then attached to the jaws of a standard tensometer where they were pulled at a cross head speed of 0.8 mm/min by applying a shear force across the joint. The force-extension data were collected by the computer via a 5 KN load cell. The shear strength was then estimated using the true contact area that was determined from the photo-micrograph by weighing a traced area on a transparent paper. The weight of tracing paper had previous been calibrated assuming uniform mass distribution. A typical force-extension data from a joint is shown Fig. 1.

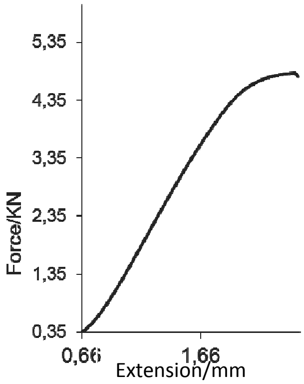

Fig. 1. Typical force extension curve

3. Results and discussion

3.1. Melting characteristics

The eutectic temperature determined for Sn-Cu system was 222°C. A near eutectic alloy Sn-0.85Cu was found to have a melting range of 222-228°C. The equilibrium eutectic temperature of this system is 226.8°C and the eutectic composition is Sn-1Cu. The near 4°C difference of the eutectic temperature recorded in this work was attributed to off-equilibrium conditions that accompanied the DSC heating at a relatively fast rate. Nevertheless the values of melting temperature range reported here were adequate to studying the soldering properties. The Sn-Ag composition with the lowest melting temperature range was Sn-7Ag which is consistent with the known equilibrium eutectic composition. The melting regime of this alloy was 224.1-226.6°C. This is in accord with the published equilibrium eutectic temperature of 220.3°C for this system. This invariant temperature of SnCu and SnAg was about 40°C higher than that of the conventional eutectic PbSn solder. A comparison of the melting temperature ranges between these systems is shown in Fig. 2.

For ternary Sn-Ag-Cu the SAC system, the alloy with the lowest melting range was the near eutectic composition, Sn-3.5Ag-0.9Cu (SAC). Fig. 2 shows that of all the selected alloys, Sn-0.85Cu alloy had the highest solidus temperature. This alloy melts at a higher temperature than the other three unleaded alloys indicated. Although the SAC-1.5Bi alloy had a slightly higher solidus temperature as compared to the SAC and Sn-7Ag solders, it has a much smaller pasty range. This rendered the SAC-1.5Bi alloy the best choice of alloy from the ones investigated, from the melting characteristics point of view. The lower melting range provides operational advantage over the hypereutectic Pb-Sn alloy as it should solidify quick to attain full strength.

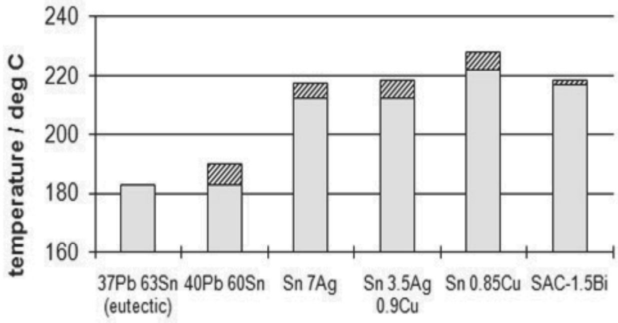

Fig. 2. Melting point range of alloys

Generally, the addition of Bi into the near eutectic SAC alloy lowered the melting point. Both the solidus and liquidus temperatures of SAC-xBi decreased with increasing concentrations of Bi, as shown in Fig. 3. It was possible for the solidus temperature to drop to values close to that of the leaded solders. However, it was observed that the melting range increased rapidly for Bi concentration exceeding 2wt%. Fig. 3 showed that up till about 10wt% Bi, the melting range was still within the acceptable range (10°C) for operational soldering. Having liquidus of around 220°C, however, did not allow the SAC-Bi alloy to have a lower operational temperature advantage over the conventional Pb-Sn ones. At 3wt% Bi, the melting range was 213.3-216.6°C which had a slightly higher solidus temperature but offered a lower liquidus temperature than the near eutectic SAC.

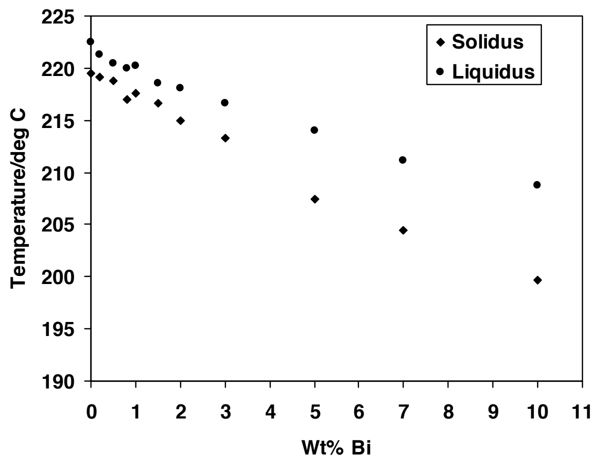

Fig. 3. Effect of Bi on the melting characteristics of SAC solder alloy

3.2. Shear strength and microstructure

The values of shear strengths determined for some selected solder alloys are shown in Fig. 4. The PbSn alloy had a shear strength of 31.0±4.7 MPa which is consistent with the known literature [1] value. Although the SAC alloy strength of 36.2 MPa was higher than that of PbSn, SAC-1.5Bi had even higher shear strength of 40 MPa. It was observed that for compositions with more that 2wt%, the shear strength decreased with increasing wt% of Bi. It is noted that for all fractured samples, failure occurred through the solder suggesting in all cases, there was a strong bond between solder and the copper substrate. The bonding of solder to the copper substrate is usually attributed to the formation of Sn-based IMC of the types Cu_6Sn_5 and (or) Cu_3Sn. Since these unleaded solders were Sn rich, the ability to bond to Cu-based substrates was retained and the wettability was good. It is understandable therefore that the mechanical integrity of soldered joints would rely entirely on the mechanical resistance provided by the solder matrix. The PbSn solders have modest strength because it relies on the morphological distribution of the Pb-Sn eutectic and the primary phases since this system have no known intermetallic compound.

On the other hand, the higher strength of the unleaded solders can be attributed to the formation of IMC. Unfavourable morphological distribution of IMC also could provide localized high stress intensity that could be the source of weakness. This provides the explanation for the lower strengths found in SAC-xBi solders with decreasing shear strengths despite the high chemical potential for formation of Cu_6Sn_5 or Cu_3Sn both of which have been shown [14] to have ultra high mechanical hardness of ~6 GPa.

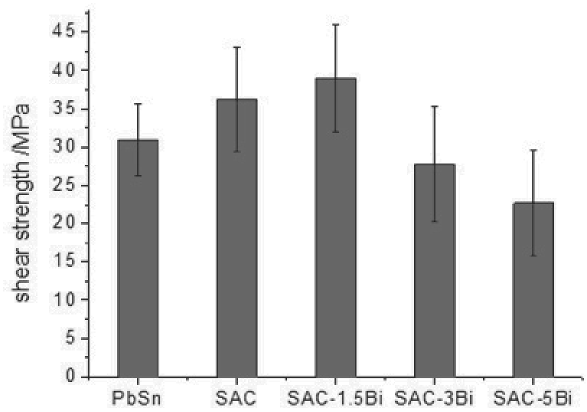

Fig. 4. Comparison of shear strength of investigated alloys

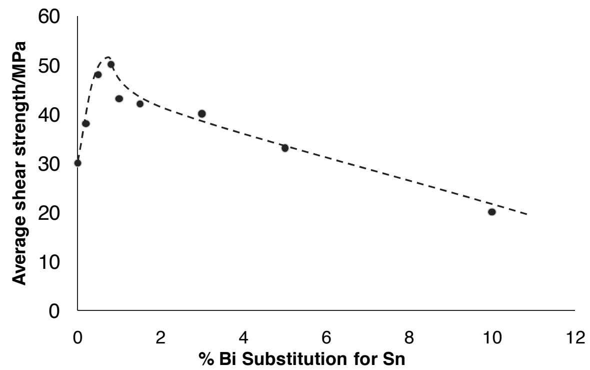

Fig. 5. Effect od Bi wt% on average shear strength of SAC alloy

a)

b)

c)

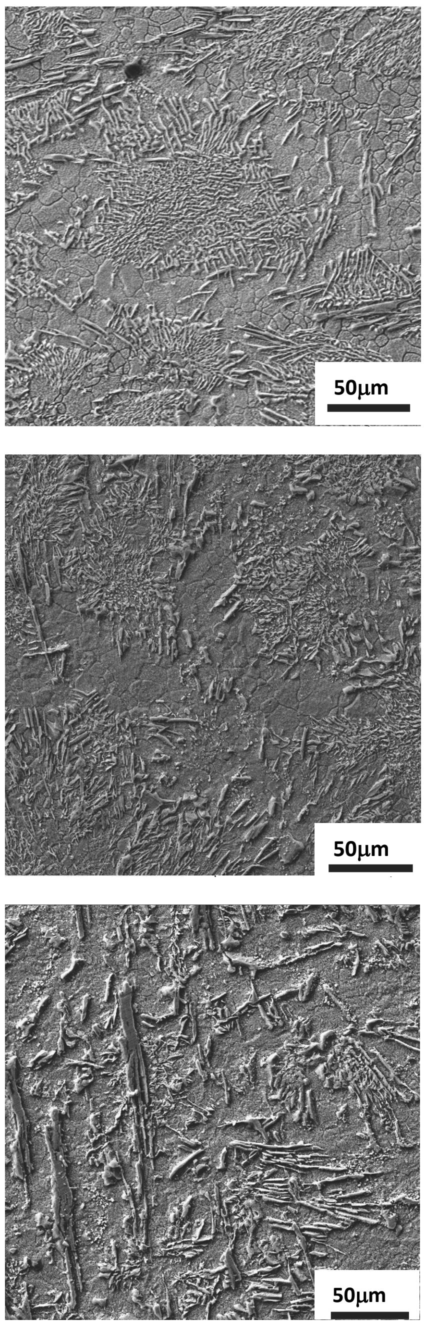

Fig. 6. Effect of Bi concentration on the morphology of Ag_3Sn (a) SAC1.5Bi, (b) SAC3Bi, (c) SAC5Bi

The effect of Bi on average shear strength is ahown in Fig. 5. Peak strengths (40-50 MPa) was found in the compositions containing 0.8 to 1.5wt% Bi. The tend observed is believed to be dictated by the role of Bi on the morphology and distribution of the dominat Ag_3Sn IMC. The effect of Bi concentration on the microstructure is shown in Fig. 6. In the SAC and the lower Bi concentration, the IMC formed islands of narrow plates with a matrix of Bi in solid solution of β- Sn. With increasing Bi content, the plate became broken down. Apart from the effect on the morphological distribution of the IMC, Bi is also very soluble in β- Sn. EDS evidence suggest up to 3wt% Bi can remain in solid solution. The implication of this would be to expect some contribution to hardening from solid solution. We found Bi rich phases in composition above and large chuncks of Cu6Sn5 IMC in compositions containing more than 5wt% Bi. It could therefore be explained that the fragmentation of the Ag_3Sn and the evolution of Bi rich phases combined to cause premature failures in compositions containing high Bi contents.

3.3. Variability in shear strength

The variability in shear strength values was followed by applying Weibull failure criteria. Though is now established that Weibull moduulus are not cosidered by it self as a material constant, it still provides ameasure of variability to expect when care is taken to keep loading condition constant. A high modulus would suggest less variability. Weibull plots were made by method described in [15]. Fig. 7 shows the Weibull plots for Pb/Sn, SAC, SAC1.5Bi and SAC5Bi. It is shown that relatively modest values of 6-7 were obtained for Pb/Sn abd SAC-1.5 while much lower value of moduls were obtained for SAC5Bi and higher concentration of Bi. This thus suggest incresed variability in assessing the shear strength of SAC with high concentration of Bi. This again is related to the role of Bi on the modification of Ag3Sn IMC and the presence of Bi rich phase.

3.4. Morphology of fractured section

The analysis of the fracture sections allows us to follow the mode of fracture and to be able to predict suitability of a solder alloy. The morphology of shear fracture sections for the selected alloys are shown in Figs. 8-12. The PbSn fracture shown in Fig. 8 is consistent with typical ductile fracture. Ductile fractures are desirable since premature failures are preventable. The ductility of this alloy stems from the fact that Pb-Sn does not form any known intermetallic compound. The morphology of fracture for Sn7Ag is shown in Fig. 9. This present a flat (almost) featureless fracture that is typical of brittle failure. This gave a high strength of 35 MPa but evidently prone to brittle failure which will reduce its reliability in appliances. The fracture section for Sn0.85Cu alloy is shown in Fig. 10. This also shows a flat surface but with small evidence of plastic deformation. This had the lowest strength and it is thought that the weakness is induced as a result of stress concentration from the Sn-Cu IMCs.

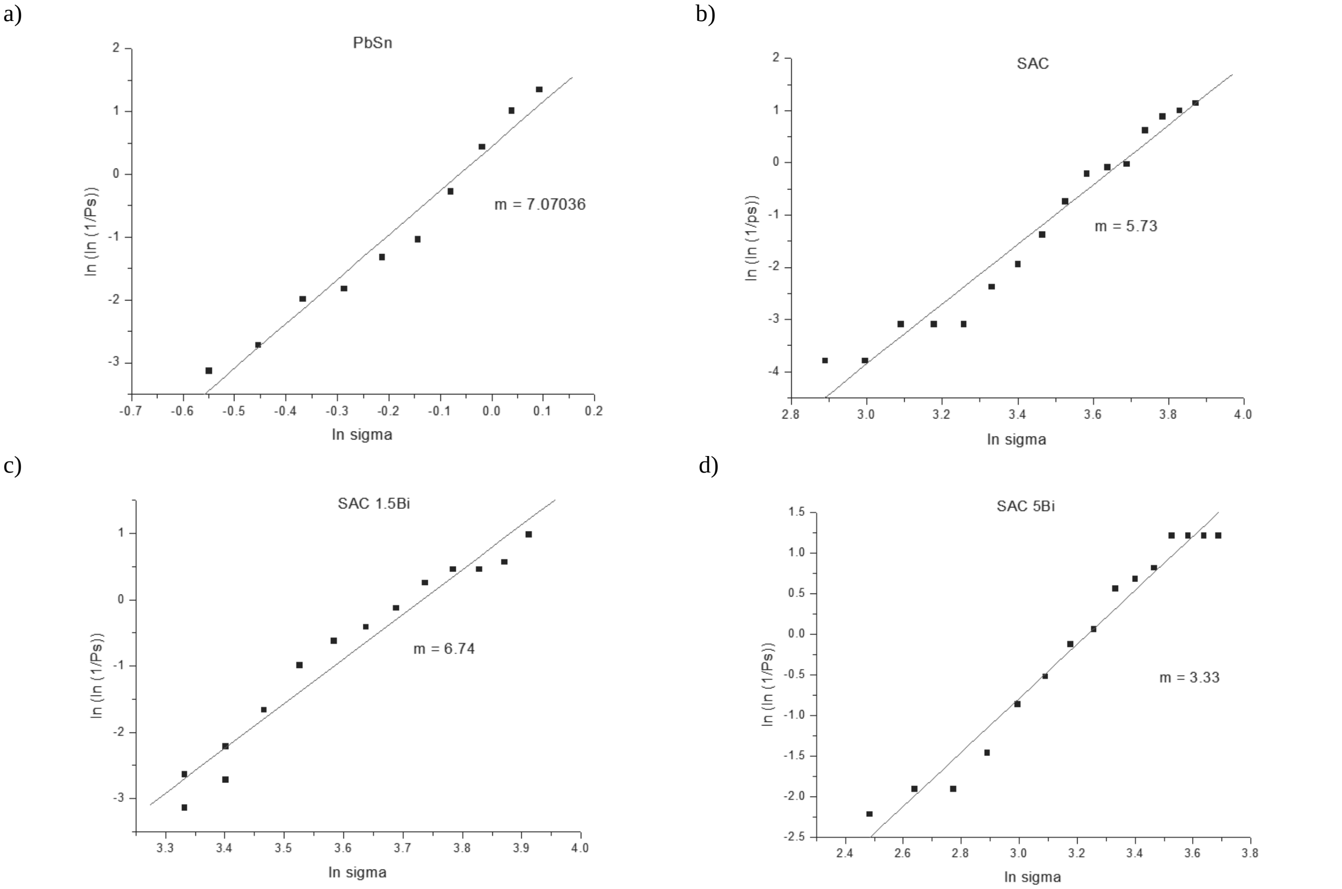

Fig. 7. Weibull Plots for the shear strength (a) Pb/Sn, (b) SAC,(c) SAC1.5Bi, (d) SAC5Bi

A microstructural investigation of the location and effects of processing of on these IMC would be useful in designing methods for improvements in mechanical properties. The fracture section for the SAC alloy is shown in Fig. 11. Here the evidence of dimpling suggests there was significant plastic deformation that means this alloys showed an appreciable ductility. It is still not as ductile as the PbSn but with the strength considerably higher. We have reported that the addition of Bi to SAC increases the strength significantly. It is interesting therefore to see whether the ductility of the SAC is still retained. The fracture morphology of SAC-0.5Bi is shown in Fig. 12. Here at much higher magnification, we see evidence of plastic micro-fracturing. At lower magnification, we observe that this is much similar to the SAC. The significant result here is that the small addition of Bi has increased the strength significantly while the ductility is not lost. The role of Bi in alloy mix is probably due to modification of the stress inducing IMCs. This needs to be confirmed by detailed studies of the microstructures.

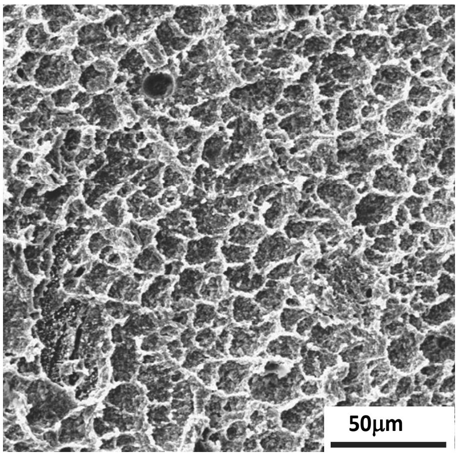

Fig. 8. Morphology of fracture for Pb-Sn alloy

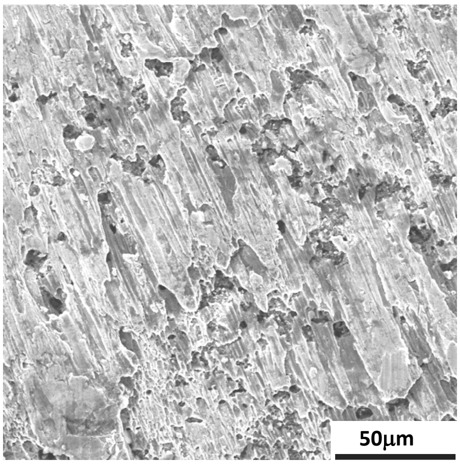

Fig. 9. Morphology of fracture for Sn7Ag alloy

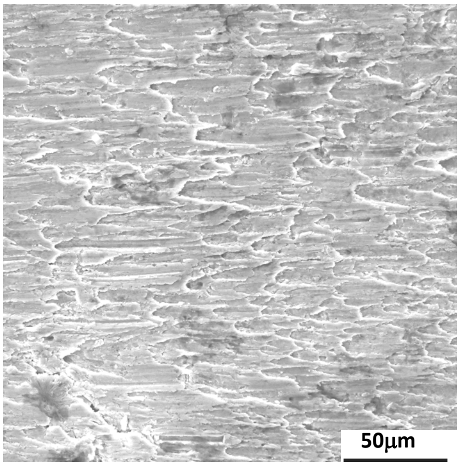

Fig. 10. Morphology of fracture for Sn0.85Cu

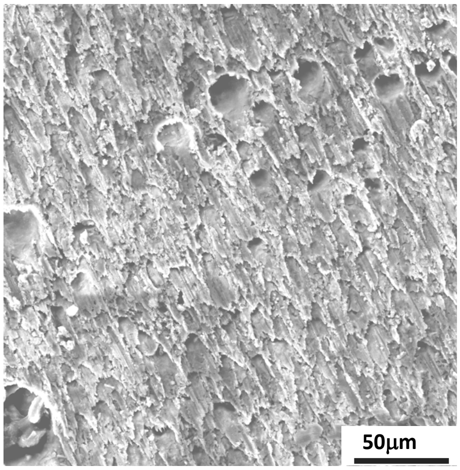

Fig. 11. Morphology of fracture for SAC

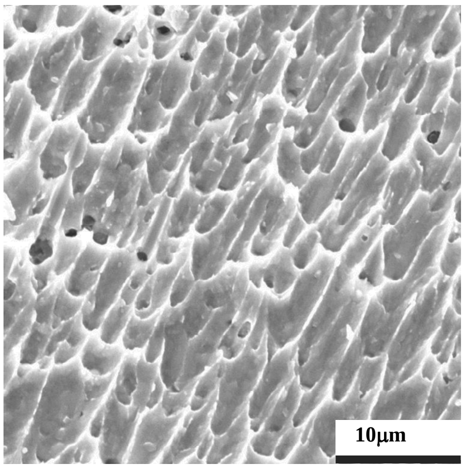

Fig. 12. Morphology of fracture for SAC 0.5Bi

4. Conclusions

The melting behaviours and the shear strength of the Sn-Ag, Sn-Cu, Sn-Ag-Cu and the Sn-Ag-Cu-Bi systems were investigated. The alloys Sn-7Ag, Sn-0.85Cu, Sn-3.5Ag-0.9Cu and Sn-3.5Ag-0.9Cu-1.5Bi were selected as the alloys that had the lowest melting points and the lowest melting ranges. All the investigated alloys were not able to achieve melting temperatures as low as the eutectic PbSn, however, alloys SAC-xBi with less than 3wt% Bi were able to achieve melting ranges as low as 2°C as well as higher shear strengths. The high strength, however, may cause the solder joint to be prone to brittle fracture. Even though the ductility of SAC-xBi becomes more desirable as wt% Bi increases, the shear strength decreases and the melting range increases. Therefore, when SAC-Bi is used, it is important to obtain a compromise. SAC alloys with the addition of less than 3wt% Bi offered properties that fall within the acceptable operational range. These include having higher shear strengths than the near eutectic SAC alloy and the conventional PbSn alloy, and lower melting range.

Acknowledgements

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