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THE ROLE OF MINOR MODIFYING ADDITIVES ON SOLDERING PROPERTIES OF SN-AG-CU GREEN SOLDERS

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ABSTRACT

With the very high rate of introducing new designs, the service lives of modern electronic devices have been dramatically shortened. This has created awareness on the implications of disposing electronic wastes with lots of leaded solders. As part of environmental compliance, the industry is now warming up to the use of non-leaded solders that are considered greener. Amongst the common choice is the eutectic of Sn-Ag-Cu (SAC) alloy which has shown great promise. Minor additions to the near eutectic SAC compositions have been used to improve some properties. Here, we have studied the effect of the addition of Bi and other refractory elements to near eutectic SAC. It is shown that minor Bi additions up to less than 2% improved the joint strengths peaking at 50 – 70MPa. EDS studies confirmed that the improvement in strength is attributable to solid solution strengthening. The strengthening effect of Bi diminishes vastly beyond 2% limit and are characterised by brittle failure at higher Bi concentrations. Thermal analyses suggest that compositions beyond 2% Bi had undergone hyper eutectic solidification that would have led to the existence of primary brittle Bi phase in the microstructure. XRD confirmed the existence of primary Bi phase in higher concentrations.

KEYWORDS

Pb-free solder, SAC, intermetallic, environmental, sustainable electronic wastes.

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 (Tu and Zheng, 2001). Pb-Sn solders have sufficiently fulfilled 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 widely used in electronic interconnects(Tu and Zheng, 2001, 2002).

With the present commercial pressures on miniaturisation of electronic devices and the very high rate of introducing new designs, the service life of modern electrical/electronic devices have been dramatically shortened. This has created awareness on the implications of disposing electronic wastes(Kidee et. al., 2013). The EU took the lead in setting the directive on the restriction of the use of certain hazardous substances (RoHS) in electrical goods. As a result of RoHS, efforts have now been devoted (see eg. Zeng, et al 2012 and Matahir et. al. 2011a, 2011b) into developing new generation of lead free interconnect alloys. Components vendors now use RoHS compliance as means of flagging the "greenness" of their products. This is however misleading as RoHS compliance does not necessarily mean a completely lead free product. The danger still exists that unless, component manufacturers completely accept unleaded solders, we will still have to deal with environmental hazards as a result of disposing electronic wastes. Though a couple of non-leaded solders alloys have been developed, component manufacturers have not truly warm up to their use. The main problem stems from lack of technical information on the long term performance of the new generation interconnects. These are susceptible to room temperature aging which put a question mark on the reliability of components made with new non-leaded interconnects.

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. A lot of efforts have therefore been devoted to the development of alloys that meet these criteria and many reviews (e.g. Zeng, et al 2012 and Laurila, T. et. al., 2010) have been published.

From the many reviews, Sn rich ternary system, Sn-Ag-Cu 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^{o}C is substantially higher than the 183^{o}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 these are susceptible to the formation of intermetallic compounds (IMC) either in the as-soldered condition or after aging. Many studies (e.g. Tseng and Duh, 2013, Tseng et. al. 2013, Pang, 2013) 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 in 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, it has been demonstrated (Keller, et al. 2011) 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 addition of Bi in SAC up to 10 wt. % has been shown (Kang, et. al., 2011) to retard the formation of interfacial IMC. This ordinarily gives a green light for use of Bi in alloy mix to stem the deleterious effect of excessive IMC growth. The use of Bi is attractive in that it forms a low temperature eutectic with Sn and Bi in a Sn rich alloy, would be expected to lower the melting temperature. Here we investigated the shear strengths of alloys centered around the composition Sn3.5Ag0.9Cu with Bi substitutions.

EXPERIMENTAL

35g of targeted compositions of ternary SAC and higher order alloys were made by melting commercially pure elements contained in a pyrex crucible under a flux of eutectic mixture of LiCl and KCl. The molten "alloy" salt provided a protective cover for the alloy melt to solidify into a clean ingot. The final compositions were confirmed using energy dispersive analysis (EDS) on the Scanning Electron Microscope (SEM). 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 set to scan at the rate of 1 ℃/min over the expected melting range. 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 universal tensile machine, where they were pulled at a cross head speed of 0.8mm/min via a 5KN load cell.

RESULTS AND DISCUSSIONS

Melting Characteristics

The melting characteristics of alloys were followed by dynamic heating in a DSC. Figure 1 shows the effects of Bi substitution for Sn in SAC alloys. The melting peaks progressively shifts to lower temperature with increasing Bi content. The peak characteristics were analysed and values of melting range (ΔT), and heat of melting reaction (ΔH) are given in Table 1. It is seen that ΔT was 3°C for SAC and for SAC alloys with Bi substitutions less that 2wt.%. For compositions with higher Bi concentrations, lager values of ΔT were evident. A melting range of 3°C is comparable to values obtained for classical binary eutectics of Sn-Cu and Sn-Ag under similar heating conditions. The melting range of 3°C observed for low concentration Bi therefore is consistent with near eutectic melting of the quaternary alloys. For same group of alloys, it is noted that ΔH averaged 65 – 70J/g, while for higher Bi content, ΔH significantly dropped to much smaller values. A comparison of ΔT with Bi content given in Table 1 gives clear divide of near eutectic melting and off eutectic melting alloys. It is evident that this divide occurs at 2wt.% Bi concentration.

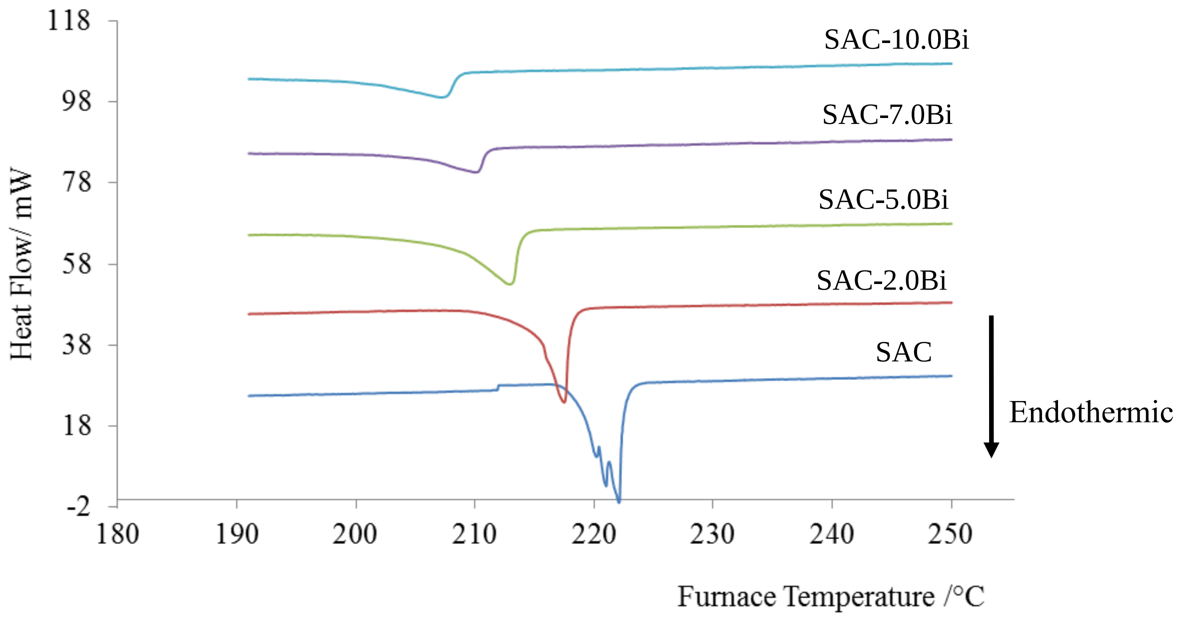

Figure 1. Effects of Bi substitution for Sn on the DSC therogram of SAC alloy

Table 1. Summary of melting characteristics of selected Pb-free solders

Alloy	Melting Temperature / °C	Temperature Range (ΔT) / °C	ΔH /J/g
SAC	219-222	3	72
SAC-0.8Bi	217-220	3	63
SAC-2Bi	215-218	3	66
SAC-3Bi	213-217	4	62
SAC-5Bi	207-214	7	57
SAC-7Bi	205-213	8	44
SAC-10Bi	200-209	9	40

The effects of minor additions of other elements on SAC-0.8Bi were studied. Here the values of ΔT and ΔH were respectively 1 – 3°C and 62 – 65J/g and are consistent with values observed for low Bi concentration SAC-Bi, thus suggesting that the addition of these modifiers did not significantly affect the melting or freezing path of the alloys.

Shear Strength

The effect of Bi substitution on the solder joint strength is represented in Figure 2. The maximum strength was observed to be 50MPa for Bi concentration of about 1wt.%. The shear strength dropped drastically once Bi substitution exceeded 2wt%. It is thought this is connected with the solidification path and the evolution of microstructure. The trend observed for the shear strength is consistent with the result of thermal analysis that showed that alloys with more than 2%Bi solidified or melt via off eutectic reaction. The implication of off eutectic solidification is that the microstructure would consist of primary phase, which in this case is thought to be Bi. The high strength observed with small Bi substitutions (<2%) is believed to be related to solid solution strengthening. However, the evolution of primary Bi for compositions that froze via off eutectic reaction, would introduce a brittle phase that would tend to embrittle the alloy and negate the hardening effect of solid solution. The evolution of primary phases has been implicated in the observed increased variability of strength values (Matahir, 20011b). Minor alloying additions of SAC-0.8Bi with Mo, Al, Ni, and Nb, actually lead to loss of solid solution induced strength. The thermal analysis did not indicate any alteration of solidification path as a result of these additions, and therefore, this effect may be related to inhomogeneity introduced by particles of these refractory elements in the solder matrix.

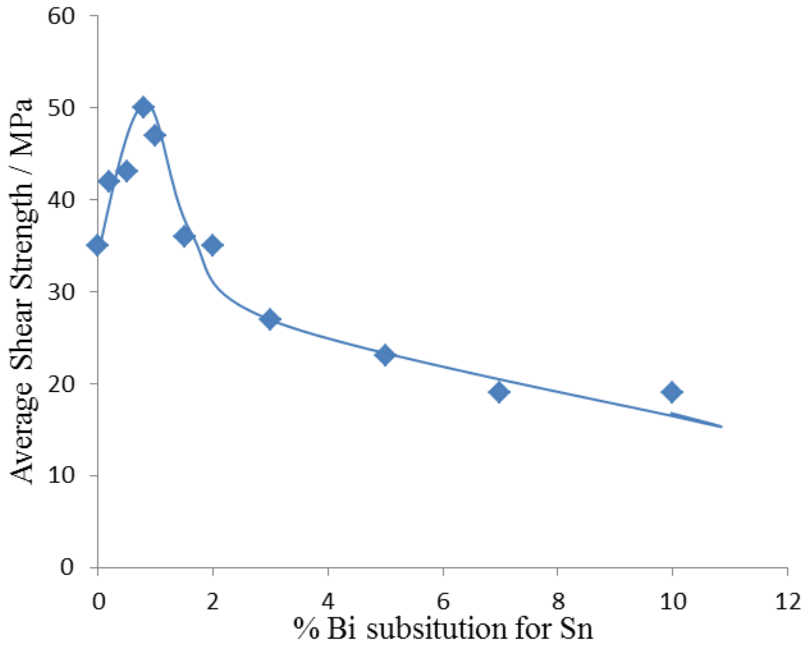

Figure 2. effect of Bi concentration on the shear strength of SAC-Bi alloys

Microstructural Evolution

Alloy ingots were observed for microstructures and this consists mostly of β-Sn and IMCs of Ag_3Sn and Cu_6Sn_5 as shown in Figure 3 for alloy SAC-0.8Bi. Though primary Bi phase is implicated for the significant drop in shear strength found in alloys containing more than 2wt% Bi, it is hard to pick up such primary phase in the microstructure because the volume proportion is small and it is expected to be finely distributed. We probed the microstructure with X-ray diffraction studies. The XRD patterns for the alloys are presented in Figure 4. It is evident that lines indicating the presence of β-Sn, Ag_3Sn and Cu_6Sn_5 as expected for near eutectic SAC. For, Alloys with more than 3%Bi, additional line indicating presence Bi is found and the intensity of the Bi line increases with Bi concentration. This XRD evidence confirmed the presence of primary Bi phase for SAC containing high concentration of Bi. Its non-detection below 3wt.% content must be related to the small volume proportion and the fine distribution of this phase. The evidence here therefore confirmed that Bi substitution of Sn beyond

2wt.% caused the alloy to solidify in an off eutectic reaction that promote the formation of primary brittle Bi phase. The existence and the fine distribution of the primary brittle Bi phase in the microstructure must have induced brittle failure and thus negate the gain in shear strength from the solid solution strengthening. This evidence therefore suggest that a much lower solubility limit (less than 2%) exist in the Sn-Bi system than previously suggested (Kattner, 2002). The present result is in accord with more recent evidence (Okamoto, 2010) for equilibrium data for Bi-Sn. The result here has implication for development of high performance Pb- free green solders and especially for SAC types where it has been advocated to add Bi for lowering melting temperatures. The work here suggest a limit of 2wt percent in order to improve strength (50Mpa) and avoid the embrittling effects with higher concentration of Bi.

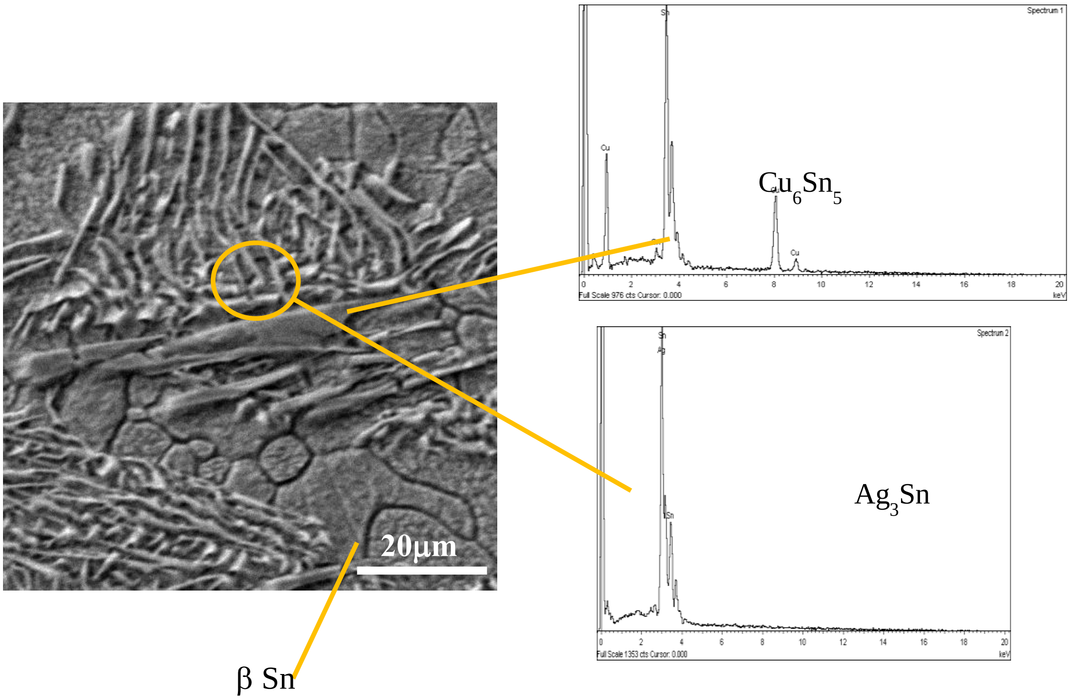

Figure 3. Typical microstructure in ingot alloy

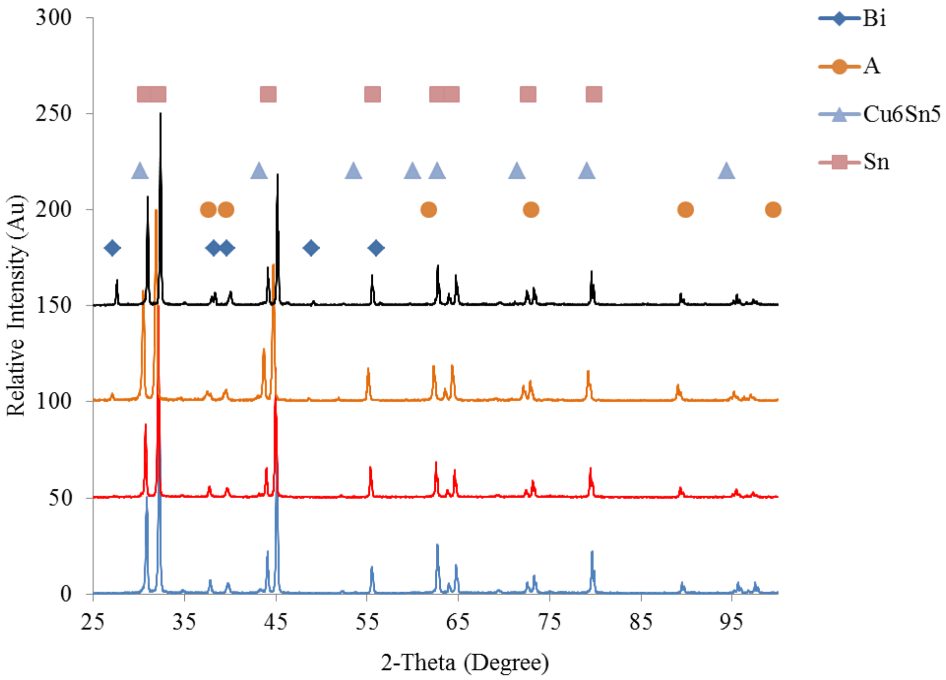

Figure 4. Effect of Bi substitution on appearance of Bi phase in ingot alloy

CONCLUSIONS

The effects of substituting Bi for Sn in SAC-xBi Pb free solder alloys were investigated. Thermal analyses suggest that progressive substitution of Bi lead generally to decrease in melting temperatures. The melting range observed were less than 3^{o}C for substitution less than 2wt% that may indicate a departure from near eutectic freezing. It is also observed that peak strength was obtained for compositions in the range of 1 – 2wt % Bi. Both XRD and EDS suggest that the peak strength observed was as result of solid solubility strengthening. Beyond 2 % concentration of Bi, the alloy must have undergone off eutectic solidification that led to the precipitation of primary Bi phases as in indicated by XRD. The presence of primary Bi phase would normally provoke premature brittle failure irrespective of amount of solid solution strengthening. The 2% solubility limit reported here is consistent with new evidence of equilibrium phase diagram presented for Sn-Bi system by Okamoto (2010). This work contributes to promoting the usability of lead free solders in electronic devices and thus supports the sustainability of high volume electronic wastes.

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