Effect of addition of Cu on the properties of eutectic Sn-Bi solder alloy

S.N. ALAM*, N. JINDAL, N. NAITHANI

Department of Metallurgical and Material Engineering, National Institute of Technology Rourkela, Rourkela, Odisha, Pin-769008, India

The present work reports the effect of Cu addition on the melting point, hardness and electrical resistivity of Sn-57 wt.% Bi eutectic solder alloy. Both binary eutectic Sn-57 wt.% Bi and ternary Sn-(57-x)Bi-xCu ($x = 0.1, 0.3, 0.5, 0.7$ and 1 wt.%) alloys containing various amounts of Cu were developed by melting casting route. The microstructure of the various solder alloys was analyzed using an optical microscope and a SEM. The variation in melting point, hardness and electrical resistivity of the Sn-Bi eutectic solder alloys with the addition of Cu was determined. The melting point of the eutectic Sn-Bi solder alloy was found to decrease up to the addition of 0.7 wt.% Cu. However, further addition of Cu led to an increase in the melting point of the alloy. Addition of Cu led to an increase in the hardness of the eutectic Sn-Bi solder alloy whereas the electrical resistivity of this alloy was found to increase up to the addition of 0.7 wt.% of Cu beyond which a decrease in the electrical resistivity was observed. A change in the microstructure of the solder alloy was observed when it was reheated above the melting temperature.

Keywords: *Sn-Bi-Cu; lead-free solder alloys; melting point; DSC/TGA*

1. Introduction

Solder joints play an important role in providing electronic connection and mechanical support in electronic devices. A eutectic or near-eutectic Sn-Pb solder has been used extensively for interconnection and packaging of electronic devices and circuits due to its low melting point, good wettability and reliability. However, the need to eliminate the use of lead (Pb) bearing solders in electronic components due to its toxic nature to both human health and environment has led to an enhanced research in the area of lead-free solders. In the last few decades, significant research has been done in the area of lead-free solders. A suitable lead-free solder which can substitute the existing Sn-Pb solder alloy should have a low melting temperature, low electrical resistivity, good wettability of Cu substrate, good resistance to mechanical and thermal fatigue, reliability and low cost [1–4]. One of the major limiting factors in the selection of lead-free solder alloys is that the entire electronics industry is accustomed

to the low melting point of eutectic Sn-Pb solder alloy ($T_m = 183$ °C) and the electronic components are designed to withstand this temperature. Therefore a lead-free solder alloy should have a melting point which is close to the melting point of the eutectic Sn-Pb solder alloy. Due to the relatively low melting point of Sn ($T_m = 231.9$ °C), Sn-based alloys are expected to be the most suitable candidates for lead-free solder alloys. A number of Sn-based eutectic solder alloys, like Sn-57 wt.% Bi, Sn-8.8 wt.% Zn, Sn-3.5 wt.% Ag and Sn-0.7 wt.% Cu, have been considered as potential candidates which could replace the conventional eutectic Sn-Pb solder alloys. Among them, the eutectic Sn-Bi solder alloy is a promising lead-free solder alloy which could replace the existing Sn-Pb solder alloy as it has a melting point ($T_m = 139$ °C) even lower than that of the eutectic Sn-Pb solder alloy. Bi has a low melting point of 274.1 °C however it has very high hardness of 70 MPa to 94.2 MPa. Its density is 9.8 g/cc and its modulus of elasticity is 31.7 GPa. It has a thermal conductivity of 8 W/(m·K) and coefficient of thermal expansion of 0.0000134 K⁻¹ [5, 6]. On the other hand, Sn has a melting point of 231.9 °C and its hardness

*E-mail: nasimulalam@yahoo.com

is 51 MPa to 75 MPa. Its density is 5.765 g/cc and its modulus of elasticity is 41.6 GPa. It has a thermal conductivity of 66.8 W/(m·K) and coefficient of thermal expansion of 0.000022 K^{-1} [7, 8].

Fig. 1a shows a binary phase diagram of the Sn-Bi system [9]. The Sn-Bi system has a eutectic composition for Sn-57 wt.% Bi (Sn-43 at.% Bi) and the eutectic reaction takes place at the temperature of 139 °C. The equilibrium phases in the eutectic composition are β -Sn and Bi. Bi has a significant solid solubility ($\sim 21 \text{ wt.}\%$ or $\sim 13.1 \text{ at.}\%$) in Sn at the eutectic temperature, however, the solubility of Bi in Sn at room temperature is only $\sim 2 \text{ wt.}\%$ [10]. Therefore, Bi precipitates in the Sn-rich phase by solid-state precipitation at low temperature. It is evident from the binary phase diagram of the Sn-Cu system in Fig. 1b that under equilibrium condition the solubility of Cu in Sn is very limited. The solubility of Cu in Sn is only 0.0063 wt.% and Sn in Cu is about 1 wt.% at the eutectic temperature of 232 °C [11, 12]. On the other hand, Bi and Cu are known to form a eutectic, however, no intermediate phases between them are known and there is only very slight mutual solid solubility at low temperatures [13]. This is evident from the binary phase diagram of the Bi-Cu in Fig. 1c. The solid solubility of Bi in Cu is very limited and the experimentally measured maximum solubility of Bi in Cu at 975 °C was found to be 0.0207 at.% [14]. The low mutual solubility between Cu and Bi is due to the different crystal structures of Cu and Bi. The crystal structure of Cu is FCC whereas the crystal structure of Bi is rhombohedral. Apart from this, the atomic radius of Cu ($1.57 \text{ \AA}$) and Bi ($1.63 \text{ \AA}$) are highly comparable which is also the reason why the mutual solid solubility between them is very limited. As Cu has a very low solubility in both Sn and Bi, therefore, it is expected that addition of a higher amount of Cu to the Sn-Bi eutectic solder alloy will lead to the accumulation of Cu at the Sn-Bi grain boundary. Fig. 1d shows the calculated liquidus projection of the Sn-Bi-Cu ternary system [15, 16]. The eutectic reaction in the ternary Sn-Bi-Cu system takes place at the temperature of 140.1 °C and at the composition of Sn-45.3 wt.%, Bi-54.6 wt.% and Cu-0.014 wt.%.

Fig. 1. Binary phase diagram of (a) Sn-Bi [9]; (b) Sn-Cu [12]; (c) Bi-Cu [13]; (d) liquidus projection for the Sn-Bi-Cu system [15].

The eutectic or near eutectic Sn-Bi solder alloy could especially be useful where low temperature soldering is required as it has a very low melting temperature. Low temperature soldering refers to soldering at a temperature in the range of 170 °C to 200 °C, as compared to the usual soldering temperatures which could be $\sim 250 \text{ °C}$. Low temperature soldering is especially useful when the electronic devices to be soldered are prone to thermal damage like in case of soldering of sensitive electronic components, step soldering or soldering of LEDs [17]. Low temperature soldering can also reduce the risk of thermal shock induced by the thermal expansion mismatch among different materials in an electronic package. Cd, In or Bi-containing solder alloys have a melting point in the range of 45 °C to 170 °C and are considered widely as low temperature solders. However, Cd is toxic in nature and In is relatively costly which is why Bi-containing solders are considered as ideal low temperature solders [18]. Due to its low melting temperature (139 °C) as compared to that of the commercial eutectic Sn-Pb (183 °C) solder alloy, the peak exposure temperature is reduced which, in turn, reduces the risk of thermally induced damages. This could effectively lower the thermal stress at the solder joint. This is why the Sn-Bi solder alloy has drawn much interest as a potential candidate for replacing the commercially available

Sn-Pb solder alloys. Apart from this, the Sn-Bi solder alloy has good joint strength and creep resistance and also does not show any shrinkage upon solidification. It has also a low coefficient of thermal expansion and low cost. However, the mechanical properties of Sn-Bi solder alloys do not meet the strength requirements of soldered joints due to inappropriate microstructure. The major concern of the Sn-Bi solder alloy is its lack of ductility and wettability. Wettability is one of the key factors in evaluating a lead-free solder. It is the ability of a solder to spread on a substrate during reflow process. The wettability of Sn-Bi eutectic solder alloy is poorer than that of the Sn-Pb solder alloy and adding alloying elements could improve the wettability of this solder alloy [8]. The contact angle of the Sn-Bi eutectic solder alloy is relatively high, as Bi is a surface active element and it has a much lower surface tension as compared to Sn. The surface tension of the liquid Sn-Bi eutectic alloy which contains a large volume fraction of Bi is much lower than that of the commercially available Sn-Pb eutectic alloy in the same state [19, 20]. The hardness of Bi (166.70 MPa) is almost double that of Sn (78.46 MPa) and Bi is also very brittle. The brittle nature of Bi also makes the solder alloy highly brittle. Apart from this, the Sn-Bi solder alloy is also heavy due to the high density of Bi and the large wt.% of Bi in the eutectic Sn-Bi solder alloy. The high density of the eutectic Sn-Bi solder alloy makes the overall weight of the device using Sn-Bi solder alloy high. However, the properties of the Sn-Bi solder alloy can be improved by adding minor elements, like Cu and Zn [21]. It has also been reported that addition of rare earth elements can refine the microstructure of the solder alloy and also improve its mechanical properties due to high chemical activity of these elements [22, 23]. Here, in the present study the effect of addition of alloying element Cu on the microstructure, hardness and electrical resistivity of the eutectic Sn-57 wt.% Bi solder alloy has been investigated.

2. Experimental

Sn-Bi eutectic solder alloy as well as various Sn-Bi-Cu alloys, were developed from Sn, Bi and

Cu having a purity higher than 99 %. Sn granules were procured from Merck, Bi was procured from Loba Chemie and Cu was procured from Rankem, RFCL Ltd. Both binary eutectic Sn-57 wt.% Bi and ternary Sn-(57-x)Bi-xCu ($x = 0.1$ wt.% Cu, 0.3 wt.% Cu, 0.5 wt.% Cu, 0.7 wt.% Cu and 1 wt.% Cu) alloys containing various amounts of Cu were developed by melting casting route. The elements were taken in the proper fraction and melted in a silica crucible in a muffle furnace in air atmosphere. The casting temperature of the solder alloys was 550 °C. The furnace was heated to the desired temperature by electrical resistance heating elements. Initially, Sn granules were melted in the crucible and later Bi and Cu were added to the molten Sn. The molten alloys were homogenized and held at this temperature for 2 h and later furnace cooled to develop the solder alloys. The morphology and elemental composition of the samples were analyzed using a JEOL JSM-6480LV scanning electron microscope (SEM) equipped with an INCAP-entaFET-x3 X-ray microanalysis system with a high-angle ultra-thin window detector and a 30 mm² Si(Li) crystal for EDX (energy dispersive X-ray spectroscopy) analysis. A Nova NanoSEM 450/FEI field emission scanning electron microscope (FE-SEM) was also used for the microstructural characterization of the alloys. Differential scanning calorimetry (DSC) was done in order to determine the melting point of the alloys. The thermal analysis of the samples was done in a Netzsch STA 409C Simultaneous Thermal Analyzer at a heating rate of 10 °C/min in Ar atmosphere. X-ray diffraction (XRD) of the alloys was done in a Panalytical PW 3040 X'Pert MPD using CuK α radiation ($\lambda = 1.54056$ Å) to find out if any new phase was formed during their development. The hardness of the samples was measured using a digital Leco Vickers microhardness tester (LV 700). The electrical resistivity of the solder alloys was measured by four-point probe method using a Keithley nanovoltmeter with DC current source. Fig. 2 displays the schematic diagram showing the four-point probe electrical resistance measurement technique. Here, V is the voltage between the inner probes, I is the current through the outer probes, s is the needle spacing and ρ_s is the sheet resistance.

In the present study the thickness of the sample was considerably higher as compared to that of the spacing s . The resistivity ρ of the sample was determined using the formula given below [24]:

$$\rho = \frac{V}{I} 2\pi s \quad (1)$$

The wettability of the various solder alloys was analyzed from the contact angles of the solder used on Cu substrate.

Fig. 2. Schematic diagram showing the four-point probe electrical resistance measurement technique.

3. Results and discussion

XRD analysis of the various solder alloys was done in order to determine the formation of any new phases. The XRD pattern of the as-cast Sn-57Bi alloy in Fig. 3a shows the presence of β -Sn and Bi. This is in complete coherence with the binary phase diagram of the Sn-Bi system in Fig. 1a which also shows the absence of any compound formed between Sn and Bi. Fig. 3b shows the XRD

plots of the various Sn-Bi-Cu solder alloys. Peaks corresponding to Cu could not be seen in any of the XRD plots of the Sn-Bi-Cu solder alloys due to the very low amount of Cu added to the Sn-Bi eutectic solder alloy. No new phases are also observed in the XRD plots of these Sn-Bi-Cu solder alloys and similar peaks as those seen in the case of the eutectic solder alloy are also seen in the XRD plots of the Sn-Bi-Cu solder alloys. The ternary phase diagram of Sn-Bi-Cu in Fig. 1d predicts the formation of intermetallic Cu_6Sn_5 , however, the peaks corresponding to Cu_6Sn_5 could not be detected in the XRD plot of any of the Sn-Bi-Cu solder alloys as the amount of the Cu_6Sn_5 phase formed is very low [25, 26]. Addition of Cu has led to grain refinement. This is evident from the diminishing intensity of the XRD peaks of Sn. Fig. 3c shows the decreasing intensity of the XRD peak of Sn at $2\theta = 37.3^\circ$.

The optical micrographs of the eutectic Sn-Bi solder alloy in Fig. 4a to Fig. 4d show the presence of dendritic β -Sn regions. Large dendrites of β -Sn can be clearly seen in all the optical micrographs. Bi diffuses out of the β -Sn dendrites resulting in occurrence of Sn-rich phase in the dendrites. This is illustrated in the schematic diagram in Fig. 4i. From the binary phase diagram of Sn-Bi solder alloy in Fig. 1a it is evident that the solid solubility of Sn in Bi is negligible although there is significant solid solubility of Bi in Sn. The maximum solid solubility of Bi in Sn is ~ 22 wt.% at the eutectic temperature. As a result Bi precipitates in the Sn-rich phase by solid-state precipitation when cooled. A well-defined eutectic microstructure could be seen in the optical micrographs in Fig. 4a to Fig. 4d as well as in the SEM images in Fig. 4e to Fig. 4h. Sn-Bi has a low-melting eutectic and is known to form a well-defined eutectic microstructure irrespective of the cooling rate. The eutectic microstructure shows two constituent alternate phases with reasonably well defined colonies. The microstructure of the eutectic solder alloy mainly consists of primary β -Sn phase and Sn-Bi eutectic phase. The microstructure shows typical short striped lamellar eutectic regions having alternate dark Bi-rich phase and white Sn-rich phase [27, 28]. The eutectic structure

Fig. 3. XRD plots of (a) Sn-57Bi eutectic and (b) various Sn-Bi-Cu solder alloys; (c) peak of Sn at $2\theta = 37.3^\circ$.

consists of network-shaped alternate dark and light regions having a complex but regular internal geometry. As the alloy had undergone slow cooling in the furnace, the eutectic regions were found to be coarse. The eutectic was found to have a composition of 78.50 wt.% Sn and 21.50 wt.% Bi. The SEM images of the as-cast eutectic Sn-57 wt.% Bi alloy in Fig. 4e to Fig. 4h show a lamellar structure. The microstructure of the binary Sn-Bi eutectic solder consists of Sn-rich dendrites surrounded by a eutectic mixture having alternate Bi-rich and Sn-rich lamellar phases. The eutectic microstructure of Sn-Bi solder alloy shows colonies that have complex but regular internal geometry.

Fig. 5a to Fig. 5c are the optical micrographs of the Sn-56.9Bi-0.1Cu solder alloy. Addition of 0.1 wt.% Cu to the eutectic Sn-57Bi solder alloy has not caused any major change in the microstructure of the solder alloy. Fig. 5d to Fig. 5h are the SEM images of Sn-56.9Bi-0.1Cu solder alloy along with the EDX analysis of various phases. The white colored bright areas in the eutectic regions are Bi-rich and contain about 96.1 at.% Bi, 2.84 at.% Sn and 1.07 at.% Cu. The dark

regions are Sn-rich and contain about 96.99 at.% Sn, 2.64 at.% Bi and 0.37 at.% Cu. The eutectic regions on a whole contain about 92.44 at.% Sn and 7.56 at.% Bi [29].

The optical images in Fig. 6a to Fig. 6d show the microstructure of the Sn-56.7Bi-0.3Cu solder alloy. The microstructure of the Sn-56.7Bi-0.3Cu solder alloy consists mainly of dendritic β -Sn and eutectic regions consisting of alternate Bi-rich and Sn-rich lamellae. The SEM images of Sn-56.7Bi-0.3Cu solder alloy in Fig. 6e to Fig. 6h indicate that the eutectic regions have refined Bi-rich and Sn-rich regions [8]. The increase in Cu content in the Sn-Bi eutectic solder alloy has resulted in the refinement of the microstructure. Addition of Cu has led to finer Bi-rich and Sn-rich lamellae in the eutectic regions. The optical images in Fig. 7a to Fig. 7d of Sn-56.5Bi-0.5Cu solder alloy also show a similar microstructure having fine lamellae of Bi-rich and Sn-rich phases in the eutectic regions. From both the optical images in Fig. 7a to Fig. 7d as well as the SEM images in Fig. 7e to Fig. 7g it is evident that addition of Cu has refined the lamellar spacing. The EDX analysis along with the SEM

Fig. 4. (a-d) optical images; (e-h) SEM images and EDX analysis of Sn-57Bi solder alloy; (i) schematic diagram showing diffusion of Bi from the β -Sn-dendrites.

Fig. 5. (a-c) optical images (d-h) SEM images and EDX analysis of Sn-56.9Bi-0.1Cu solder alloy.

image in Fig. 7g of the eutectic region suggests a much higher amount of Sn dissolved in the light colored Bi rich region along with a small amount of Cu (78.48 at.% Bi, 20.21 at.% Sn, 1.31 at.% Cu) and also a higher amount of Bi dissolved in Sn is also observed in the dark colored Sn rich region along with a small amount of Cu (94.41 at.%

Sn, 4.23 at.% Bi, 1.35 at.% Cu). Addition of higher amount of Cu to the eutectic Sn-Bi solder alloy has led to an increase in the solid solubility of Sn in Bi as well as Bi in Sn [30].

The EDX analysis along with the SEM images in Fig. 8h and Fig. 9g of Sn-57Bi-0.7Cu and Sn-57Bi-1Cu solder alloys, respectively clearly

Fig. 6. (a-d) optical images (e-h) SEM images of Sn-56.7Bi-0.3Cu solder alloy.

Fig. 7. (a-d) optical images; (e-g) SEM images and EDX analysis of Sn-56.5Bi-0.5Cu solder alloy.

shows the formation of Cu_6Sn_5 intermetallic compound when a higher amount of Cu is added to the eutectic Sn-Bi solder alloy. Intermetallic Cu_6Sn_5 can be seen when the amount of Cu is higher than 0.5 wt.% in the Sn-Bi-Cu solder alloy. Highly stoichiometric Cu_6Sn_5 intermetallic compound (55.23 at.% Cu, 44.68 at.% Sn, 0.09 at.% Bi) can be seen in the SEM image in Fig. 8h. Trace amount of Bi are also seen in the intermetallic compound. The Cu_6Sn_5 intermetallic compound was found to have sharp edges. They are very few in number and have large cross-sectional width of $\sim 244 \mu\text{m}$. An increase in the concentration of Cu not only results in the formation of Cu_6Sn_5 intermetallic compound but also a larger number of β -Sn dendrites can be seen. This suggests that Cu hinders the formation of Sn-Bi eutectic [14, 31].

Fig. 9a to Fig. 9c show the optical images of the Sn-56Bi-1Cu solder alloy and Fig. 9d to Fig. 9g show the SEM images of the Sn-56Bi-1Cu solder alloy along with EDX analysis of different phases in the microstructure. The bright white colored regions in the SEM image in Fig. 9g are Sn-rich regions (90.06 at.% Sn and 9.94 at.% Bi), whereas the slightly dark colored regions are the eutectic regions (57.87 at.% Sn, 41.95 at.% Bi and 0.18 at.% Cu). This region is made of fine bright white colored Sn-rich lamellae and dark colored Bi-rich lamellae adjacent to each other. The interlamellar spacing has been found to be finer with the increase in the addition of Cu. As the amount of Cu in the eutectic Sn-Bi alloy increases, the volume fraction of the β -Sn in the alloy increases. The microstructure coarsening is substantially reduced

Fig. 8. (a-d) optical images; (e-h) SEM images and EDX analysis of Sn-56.3Bi-0.7Cu solder alloy.

Fig. 9. (a-c) optical images; (d-g) SEM images and EDX analysis of Sn-56Bi-1Cu solder alloy.

by the addition of Cu into the binary Sn-Bi solder alloy. Grain size refinement is also evident from the diminishing intensity of the Sn peaks in the XRD plot in Fig. 3c [32].

The DSC plot in Fig. 10a of Sn-57 wt.% Bi solder alloy shows a sharp endothermic peak at $\sim 150.98^\circ\text{C}$ which corresponds to the melting point of the eutectic Sn-Bi solder alloy. The reported melting point of the eutectic Sn-57 wt.% Bi composition given in literature is 139°C [33]. The slight difference between the two temperatures may be due to the oxide formed during the development of the eutectic alloy or any other impurities in the alloy. Fig. 10b to Fig. 10f are the DSC plots of the various Sn-Bi-Cu solder alloys. There is a slight decrease in the melting point of the Sn-Bi eutectic

solder alloy with the addition of 0.1 wt.% Cu. Further addition of Cu up to 0.7 wt.% does not have any effect on the melting temperature of the alloy. Fig. 11a shows the variation in melting point and Fig. 11b shows the variation in the width of the mushy zone of Sn-Bi eutectic solder alloy with the addition of Cu. The initial reduction in the melting temperature of the solder can be attributed to the increase in the surface instability with high surface free energy which is induced by the addition of Cu. The lowering of the melting point of the Sn-Bi solder alloy by addition of 0.1 wt.% Cu has also been reported by Shen et al. [34]. A rise in the melting point of the solder alloy is observed beyond the addition of 0.7 wt.% of Cu. This can be attributed to the higher weight fraction of Cu which

Fig. 10. DSC plots of pure Sn-Bi eutectic and various Sn-Bi-Cu solder alloys.

has a higher melting point (1085 °C). Also it should be noted that intermetallic compound Cu_6Sn_5 having high melting point is also formed when more than 0.5 wt.% Cu is added to the eutectic Sn-Bi solder alloy. The variation of the mushy zone also shows a similar trend as that of the melting point. The mushy zone is a region where both liquid and solid phase co-exist during melting or solidification of a metal or alloy generally adjacent to the liquid-solid interface. With the start of melting, the melt flow may lead to a mainly dendritic mushy zone. Addition of Cu increases the mushy zone. The mushy zone comprises of two interpenetrating phases [35–37]. It consists of a solid phase and void space. The interconnected voids are occupied by a liquid molten metal which flows through the void space. Fig. 12 displays a schematic diagram showing the liquid and solid phases in the mushy region.

Fig. 13a shows the variation of hardness with the addition of Cu in the Sn-Bi eutectic solder alloy. The plot in Fig. 13a clearly indicates an increase in hardness of the Sn-Bi eutectic solder alloy with the increase in Cu content. Addition of Cu to the Sn-Bi eutectic leads to segregation of Cu at the grain boundaries. The increase in hardness of the eutectic Sn-Bi solder alloy is due to the grain boundary pinning. The sudden rise in the hardness when 1 wt.% Cu is added to the eutectic Sn-Bi solder alloy is due to the formation of

the intermetallic compound Cu_6Sn_5 . The formation of intermetallic Cu_6Sn_5 is observed only when a higher amount of Cu is added. The formation of Cu_6Sn_5 is also confirmed by the SEM images of Sn-56.3Bi-0.7Cu and Sn-56Bi-1Cu solder alloys in Fig. 8h and Fig. 9g, respectively. Intermetallic compounds are hard and brittle and formation of the intermetallic compound leads to an increase in hardness of the solder alloy.

Fig. 13b shows the variation of electrical resistance ρ of eutectic Sn-Bi solder alloy with Cu content. The electrical resistivity of the eutectic Sn-Bi solder alloy is found to increase with the addition of up to 0.7 wt.% of Cu thereafter, on further addition of Cu, the resistivity of the solder alloy decreases. As Cu has a very low electrical resistivity ($1.68 \times 10^{-6} \Omega\text{-cm}$) [38, 39] therefore it is expected that the addition of Cu will reduce the electrical resistivity of the eutectic Sn-Bi solder alloy. Initially, the increase in the electrical resistivity with the addition of Cu into the Sn-Bi eutectic solder alloy is attributed to the scattering of electrons by the random distribution of the Cu atoms. This is also predicted by the Nordheim rule [40, 41]. The Sn-56.5Bi-0.5Cu and Sn-56Bi-1Cu solder alloys were later used as a solder on a Cu substrate and the microstructure of the soldered alloy was observed under a SEM. Fig. 14 shows the SEM images of Sn-56Bi-1Cu solder alloy after reheating and use as solder on Cu substrate. The Sn-Bi-Cu solder alloy

Fig. 11. Variation of (a) melting point and (b) width of the mushy zone of Sn-Bi eutectic solder alloy with Cu content.

Fig. 12. Schematic diagram showing the mushy region.

shows microstructural instability on being reheated above the melting point [14]. Noticeable changes in the microstructure can be observed when the Sn-Bi-Cu solder alloy is reheated to be used as a solder. On soldering, it is evident that there is substantial coarsening of the microstructure. The fine lamellar structure of the as-cast solder alloy is not seen anymore. The elemental maps of Sn and Bi in Fig. 15c and Fig. 15d, respectively, in the Sn-56.5Bi-0.5Cu solder alloy after reheating and use as solder on Cu substrate also shows very large Sn grains. Sn has a slightly lower melting point of 231.9 °C as compared to Bi which melts at 271.4 °C so it is expected that smaller grains of β -Sn will fuse to grow into larger Sn grains. Also, the eutectic microstructure seen earlier does not show the usual lamellar pattern. The dendrites of β -Sn have grown and interconnected forming large regions of Sn-rich regions thereby diminishing the Bi-rich regions which are found to be trapped between the Sn-rich regions. The composition of the Sn-rich region is 94.33 wt.% Sn and 5.67 wt.% Bi, whereas the composition of the Bi-rich region is

80.83 wt.% Sn and 18.74 wt.% Bi and 0.42 wt.% Cu. Cu could only be traced in the Bi-rich region [42].

From the optical images in Fig. 16, it is evident that the wettability of the Sn-Bi-Cu solder alloy is low. It does not flow and spread but tends to form beads on the Cu substrate leading to a high angle of contact. Miao et al. [10] reported that the addition of 1 wt.% of Cu did not influence critically the wettability of the Sn-Bi eutectic solder alloy. The SEM images in Fig. 16f and Fig. 16g show 56.5Bi-0.5Cu and Sn-56Bi-1Cu solder alloy used on Cu substrate, respectively. The SEM image in Fig. 16f clearly shows high contact angle at the interface of the Sn-56.5Bi-0.5Cu solder alloy and the Cu substrate whereas the SEM image in Fig. 16g shows edges of the solder lifting from the Cu substrate. The addition of Cu was not found to have any effect on the wettability of the eutectic Sn-Bi solder alloy.

4. Conclusions

1. Increase in the amount of Cu in the Sn-Bi eutectic solder alloys has led to finer lamellae of the Sn-Bi eutectic regions and also reduced the interlamellar spacing.
2. Addition of higher amount of Cu in the Sn-Bi eutectics has led to an increase in the hardness of the Sn-Bi eutectic solder alloy due to the grain boundary pinning effect of Cu. Formation of eutectic regions having finer lamellae as well as the formation

Fig. 13. Variation of (a) hardness and (b) electrical resistance of eutectic Sn-Bi eutectic solder alloys with Cu content.

Fig. 14. SEM images of Sn-56Bi-1Cu solder alloy after reheating and use as solder on Cu substrate.

of Cu_6Sn_5 intermetallic compound has also led to the higher hardness of the Sn-Bi-Cu solder alloy.

3. The width of the mushy zone of the Sn-Bi eutectic solder alloy initially shows a decrease up to the addition of 0.7 wt.% Cu. However, addition of Cu beyond 0.7 wt.% caused a sudden increase in the width of the mushy zone.
4. A change in the microstructure of solder alloy is observed when it is reheated above the melting temperature. An increase

in the Sn-rich β -Sn regions is observed with the shrinkage in the area of Bi-rich regions. The lamellar structure undergoes a complete rearrangement in many regions of the solder alloy.

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Fig. 15. (a) SEM image and elemental maps of (b) Sn + Bi (c) Sn and (d) Bi in Sn-56.5Bi-0.5Cu solder alloy after reheating and use as solder on Cu substrate.

Fig. 16. Optical images showing the wettability of (a) Sn-56.9Bi-0.1Cu; (b) Sn-56.7Bi-0.3Cu; (c) Sn-56.5Bi-0.5Cu; (d) Sn-56.3Bi-0.7Cu; (e) Sn-56Bi-1Cu solder alloy when used on Cu substrate. SEM images showing (f) 56.5Bi-0.5Cu and (g) Sn-56Bi-1Cu solder alloy used on Cu substrate; (h) schematic diagram showing low and high wetting angle.

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