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Experimental Investigation on the Effect of Ag Addition on Ternary Lead Free Solder Alloy –Sn–0.5Cu–3Bi

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Abstract

Lead cannot be used in the solder material anymore due to environmental legislations which is related to the inherent toxicity of lead. This paper investigates the effect of silver (Ag) addition on the melting behavior, microstructure, and microhardness of Ternary lead free solder alloy Sn–0.5Cu–3Bi. The contact angle between Sn–0.5Cu–3Bi and Cu-substrate were also analyzed. Samples with different Ag percentages (0, 0.25, 0.5, 0.75 and 1.0 wt%) in Sn–0.5Cu–3Bi were prepared using an induction furnace, annealing furnace with argon gas. Tests were conducted for melting temperature using TG–DTA analysis, chemical composition using ICP–OES, Hardness using Vickers's hardness tester and the microstructure using Field emission scanning electron microscopy. The obtained results were thoroughly analyzed. The results show that the Ag addition has striking positive effects on enhancing the properties of the base solder alloy. Melting point is found to be decreasing with the increase in Ag content. Hardness and contact angle were improved with the addition of Ag. The microstructure observations revealed that the Ag was uniformly distributed on the surface of the solder matrix. The recommended content of the Ag to be added into the Sn–0.5Cu–3Bi solder alloy is 1.0 wt%. With the observed better properties it can be considered as the potential alternative to lead–tin alloy.

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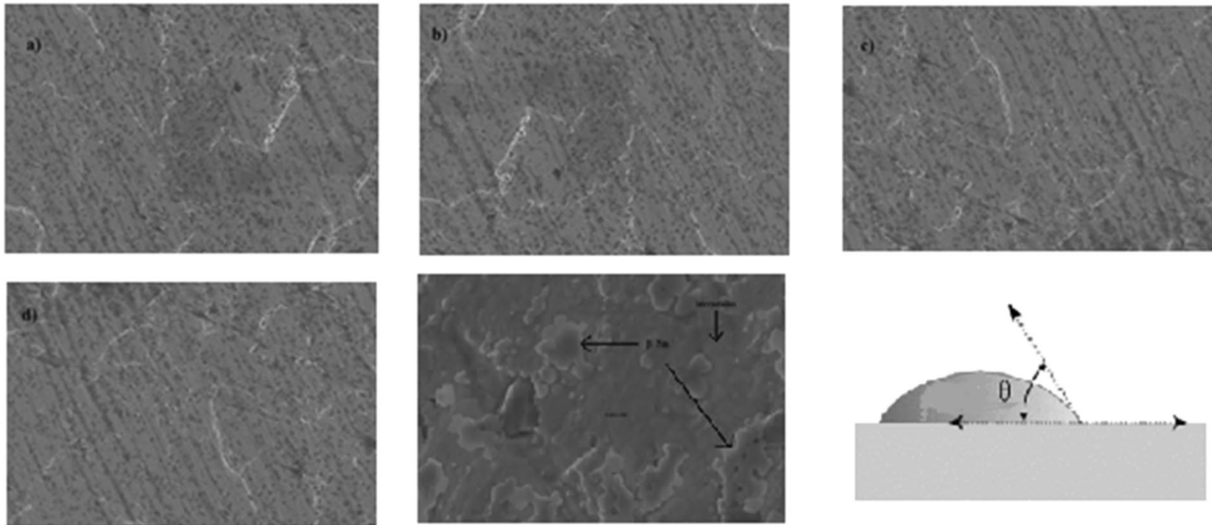
Graphical Abstract

Solder Alloy	Sn (%)	Cu (%)	Bi(%)	Ag(%)	Melting Temperature (° C)	Contact angle (°)	Hardness (Hv)
Sn-0.5Cu-3Bi	96.5911	0.4901	2.9187	0	231.15	28.74	19.8
Sn-0.5Cu-3Bi -0.25Ag	96.3417	0.4832	2.9272	0.2478	230.13	27.53	20.7
Sn-0.5Cu-3Bi -0.5Ag	95.9127	0.5132	3.0649	0.5091	229.34	26.44	21.8
Sn-0.5Cu-3Bi -0.75Ag	95.8392	0.5071	2.9048	0.7488	228.92	25.12	22.76
Sn-0.5Cu-3Bi -1Ag	95.5578	0.4973	2.9274	1.0174	226.93	24.87	24.2



Keywords Lead free · Wettability · Microstructure · Solder alloy

1 Introduction

Soldering is a widely used joining process consuming solder materials having melting point less than 315 °C [1]. Solder materials are metal alloys that are used to join or form bond between two or more components in electronics assembly to physically hold the components together in the electronic industry [2]. A solder material melts and undergoes metallurgical changes during soldering process. Apart from that it must allow contraction and expansion of various components. It must be designed to transmit electric signals and should be able to dissipate the heat generated [2]. The bonding action is achieved by melting solder material which is made to flow over and make contact with the components to be joined. A physical bond with these components is achieved on solidification. Sn–Pb (63Sn–37Pb) is a very common solder material composition with a lowest melting temperature of 183 °C [3, 4]. Due to environment concerns related to the high toxicity of lead and strict government legislations such as European Union (EU) Waste of Electronic and Electrical Equipment (WEEE) and restriction of hazardous substances (RoHS), the use of lead (Pb) is strictly prohibited in almost all electronic components [5, 6]. As a part of this restriction many researches were carried out throughout the globe to find a substitute for Sn–Pb solder alloy. Many compositions were discovered

Table 1 Composition of the solder alloy samples

Solder alloy	Sn	Cu	Bi	Ag
Sn–0.5Cu–3Bi	96.5	0.5	3	0
Sn–0.5Cu–3Bi–0.25Ag	96.25	0.5	3	0.25
Sn–0.5Cu–3Bi–0.5Ag	96	0.5	3	0.5
Sn–0.5Cu–3Bi–0.75Ag	95.75	0.5	3	0.75
Sn–0.5Cu–3Bi–1Ag	95.5	0.5	3	1

which find as a replacement for Sn–Pb alloy which were discussed in the review paper [7]. Some major composition includes Sn–Bi–Ag [8], Sn–Bi [9], Sn–Zn [10], Sn–Ag–Cu [11, 12], Sn–Cu [3, 13], Sn–Zn–Bi [10]. This paper introduces 96.5Sn–0.5Cu–3Bi as the base alloy. To this alloy Ag is added in four different quantities Sn–0.5Cu–3Bi–xAg (0.25, 0.5, 0.75, 1 wt%). Many studies have proved that the addition of foreign particles improves the microstructural and mechanical properties [14–18]. In past years, many researches has been conducted on the effect of Bi addition to different lead-free solder materials and found that the addition of Bi improves the wettability and spreading property [17, 19–27]. The electronics applications and complexity is increasing day by day. According to Moore's law 'the transistor density of integrated circuit will double in every 18 months'. From [28] it is seen that the addition of Bi has a positive effect on decreasing the melting point of Sn–0.3Ag–0.7Cu. But the addition of Bi has resulted in an increase in the melting range between liquidus and solidus which may have a chance of solidification crack. A positive wetting character enhancement is seen in the SAC157 on the addition of Bi. From [29] a drastic change is observed in the β-Sn grain surrounded by the eutectic region which was large in number to a large number of Ag_3Sn and Cu_6Sn_5 particles. Melting temperature is found to be decreasing with the addition of Bi to SAC157. 1 wt% Bi addition to SAC157 resulted in the formation of small needle-like Ag3Sn and plate-like C6Sn5 phases and enlarged eutectic area, which raised the mechanical strength and Young's modulus of SAC157 solder to about 1.5 times. Some fine Bi particles are found to disperse uniformly in a nearly pure Ag and Cu elements. The microstructure does not change significantly with the addition of 3 wt% Bi as the Sn-rich phase can dissolve a large amount of Bi [30].Bi precipitates played a significant role for enhancing the thermal and mechanical properties of SAC157 solder [30].This paper considers solder materials used in electronic packages which are exposed to relatively high temperatures like electronic packages used in automobile applications, engines etc. The melting temperature, hardness, wetting characteristics and micro structure evaluation is investigated in this paper.

2 Experimental Procedures

2.1 Sample Preparation

Solder alloy specimens were produced from pure metals which were in the powder form. The composition and assigned codes are provided in the Table 1. Pure metals of Sn, Cu, Bi and Ag in the form of powder are weighed in proper weight proportions. These were melted in induction furnace at more than 900 °C for 45 min. Then these were transferred to cylindrical molds. Five samples were made using the above procedure. The samples were quenched and were kept at room temperature for 1 day. The first sample was made using Sn, Cu and Bi according to the composition shown in the Table 1. In the next four samples Ag is added in four different proportions (0.25, 0.5, 0.75, 1 wt%). Thus samples were obtained in the form of disc shapes. Finally these samples were undergone visual inspection to ensure that the surface of these samples were free from damages.

2.2 Melting Temperature Analysis

For the development of new lead free solder alloys, melting temperature is the most vital factor to be considered. Preference will be more for a low melting temperature alloy. Melting temperature analysis of all the five samples (one sample of Sn–Cu–Bi and four samples of Sn–Cu–Bi–xAg) were conducted using thermo gravimetric and differential thermal analysis (TG–DTA). Thermo gravimetric analysis (TGA) measured the weight loss or gain as a function of temperature, the TGA trace appear as steps, it can be deal with the derivative of TGA with respect to time or temperature. Differential thermal analysis (DTA) is a technique for recording the difference in temperature between a substance and a reference material as a function of time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

Table 2 Chemical composition of the samples and the results obtained for melting temperature, hardness and contact angle

Solder alloy	Sn (%)	Cu (%)	Bi (%)	Ag (%)	Melting temperature (°C)	Contact angle (°)	Hardness (Hv)
Sn–0.5Cu–3Bi	96.5911	0.4901	2.9187	0	231.15	28.74	19.8
Sn–0.5Cu–3Bi–0.25Ag	96.3417	0.4832	2.9272	0.2478	230.13	27.53	20.7
Sn–0.5Cu–3Bi–0.5Ag	95.9127	0.5132	3.0649	0.5091	229.34	26.44	21.8
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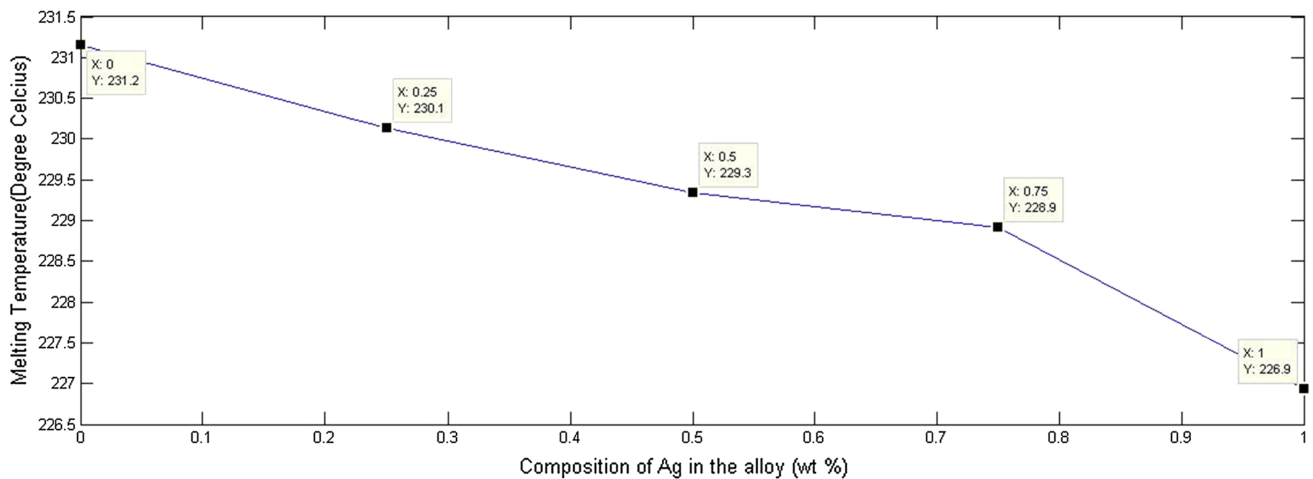


Fig. 1 Comparison of melting temperatures of the alloy samples

2.3 Hardness Test

Resistance to plastic deformation of a material is known as the hardness of that material. It is a mechanical technique which involves application of load (through indenter) onto the surface of the sample. Hardness tests were performed using HMV-G micro Vickers hardness tester. Each Hv value was the average of ten different readings which were taken at random points on the surface of the sample. For hardness tests to be performed on the sample, the surface should be smooth. Sample preparation was done using grinding by taking different grades of SiC papers. Then the samples were polished. The surfaces of the alloys were analyzed in Axio Vertical A1 metallurgical microscope before and after the microhardness test.

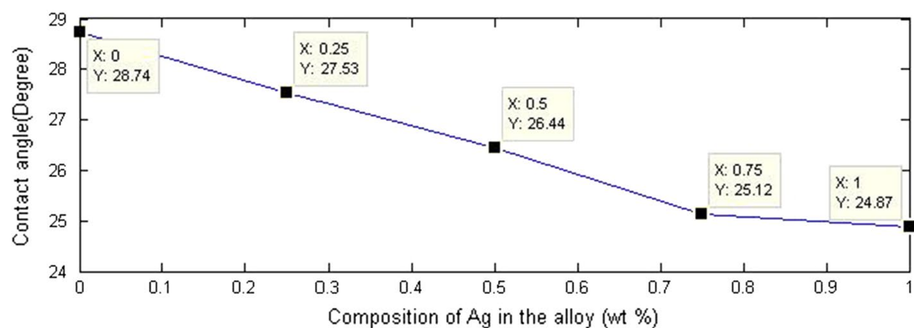
2.4 Wettability Studies

Capacity of molten solder to react with the bottom substrate is referred to as wetting. It forms a certain amount of intermetallic compound that acts as an adhesion layer to join the solder and the substrate. The reaction between the solder and substrate is important as it may affect the micro structure. It will also affect the mechanical strength of the solder joint. Here the molten sample is spread on the Copper substrate. Then the contact angle is measured. Generally if the wetting or contact angle lies between 0° and 90° the system is said to be wet. If the wetting or contact angle is between 90° and 180° the system is considered to be non-wetting [4]. In more detail if $0° < \theta < 30°$ it is considered as very good wetting, if $30° < \theta < 40°$ it is considered as good wetting, if $40° < \theta < 55°$ it is considered as acceptable wetting, if $55° < \theta < 70°$ it is considered as poor wetting and $\theta > 70°$ is considered as very poor wetting, where θ is the contact angle.

2.5 Microstructure Analysis

All the five samples were ground with four grades of SiC papers and then mechanically polished with a diamond suspension. Chemical etching was done on the alloys using 95% ethanol solution/5% hydrochloric acid. The surface details of the samples were analyzed by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Sigma). All the images were taken at a magnification of 5.00 K X,

Fig. 2 Comparison of contact angles of the alloy samples



scale = 1 µm, electron high tension (EHT) = 5.00 kV, working distance (WD) = 3.2 mm.

3 Results and Discussion

3.1 Chemical Composition

Five alloy samples were made with different composition. Chemical compositions of the alloys were analyzed using ICP–OES (Inductively coupled plasma–optical emission spectrometry). The results of the analysis are shown in the Table 2.

3.2 Melting Temperature

The soldering temperature depends on the melting temperature of the soldering alloy. Therefore the melting temperature is considered as a critical solder characteristic. A higher soldering temperature is not recommended because the higher temperature may lead to the damage of the electronic package. The melting points of all the five samples were tested using TGA analysis. The results were noted down and a comparison is shown in the Fig. 1. It can be seen that the melting temperature of Sn–Cu–Bi alloy is 231.15 °C. The melting temperature of Sn–Cu–Bi–xAg (x = 0.25, 0.5, 0.75, 1 wt%) are 230.13 °C, 229.34 °C, 228.92 °C, 226.93 °C respectively. So it can be concluded that with the addition of Ag into Sn–Cu–Bi, the melting temperature is decreasing (by almost 2% with addition of 1 wt% Ag). Bi atoms could endorse the solidification process of solder promptly through the heterogeneous nucleation at Bi particles which results in the fine microstructure and random distribution of eutectic colonies [29].

The Ag added into the Sn–0.5Cu–3Bi is found to be uniformly distributed in the solder matrix. Melting temperatures of a single material are the characteristic properties that are subject on the interatomic distance and the root mean vibration amplitude. The formation of Ag_3Sn in the matrix has altered the above properties which resulted in the decrease of melting temperature on addition of Ag incrementally. The reinforcement addition could alter the surface instability and the variation in the physical properties and the grain boundary characteristics. The degree of undercooling is the one of the key factors that affects the development and growth of intermetallic compounds. The undercooling of Sn–0.5Cu–3Bi solder material is meaningfully reduced with the addition of Ag. The results shows that the addition of Ag has a greater effect on the undercooling behavior of Sn–Cu–Bi solder. The addition of Ag cease the β-Sn dendrite growth rate. The microstructure gets refined. In other words the melting temperature is decreasing with the addition of Ag into Sn–0.5Cu–3Bi.

3.3 Wettability

Contact angle as a function of Ag addition to the Sn–Cu–Bi solder is shown in the Fig. 2. It can be seen that the contact angle of Sn–Cu–Bi alloy is 28.74°. The contact angle of Sn–Cu–Bi–xAg (x = 0.25, 0.5, 0.75, 1 wt%) are 27.53°, 26.44°, 25.12° and 24.87° respectively. Therefore, the contact angle is getting reduced as the Ag is added (by almost 13.5% with addition of 1 wt% Ag). Since $0° < \theta < 30°$ represents good wetting property, the addition of Ag is improving the wetting behavior significantly. The effect of the Ag in the molten solder is the reason for these improvements. It acts as an agent to bring down the surface tension of the alloy. It results in the upsurge in the wettability between Cu substrate. The phenomenon could be due to the decreased surface tensions of the molten solder in the presence of Ag. In this the liquid–solid and liquid–vapor surface tensions are lessened. The higher Ag concentrations reduced the viscosity of the molten solder, which is resulting in the decline in the contact angle.

3.4 Microhardness Test

The abrasion behavior and wear of a solder material can be easily analyzed using the microhardness property values. The fitness of these alloys for various applications can also be discovered using this analysis. All the five samples were undergone microhardness analysis. The analysis was done to

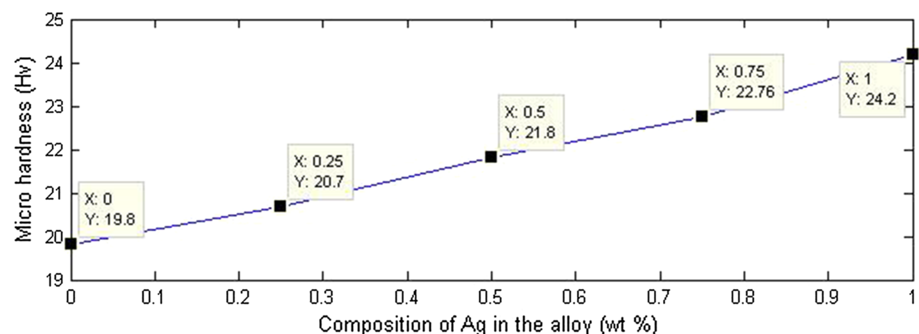


Fig. 3 Comparison of hardness values of the alloy samples

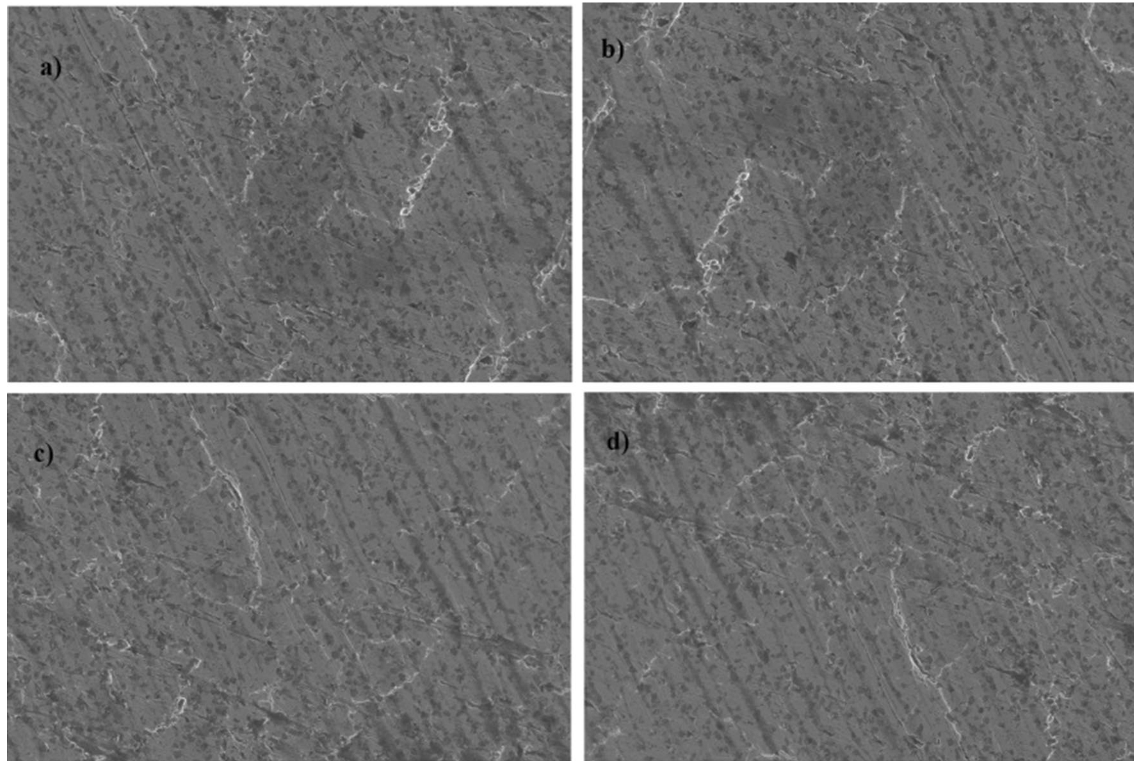


Fig. 4 FE SEM images (at 2.5 K) of **a** Sn–0.5Cu–3Bi, **b** Sn–0.5Cu–3Bi–0.25Ag, **c** Sn–0.5Cu–3Bi–0.5Ag and **d** Sn–0.5Cu–3Bi–0.75Ag

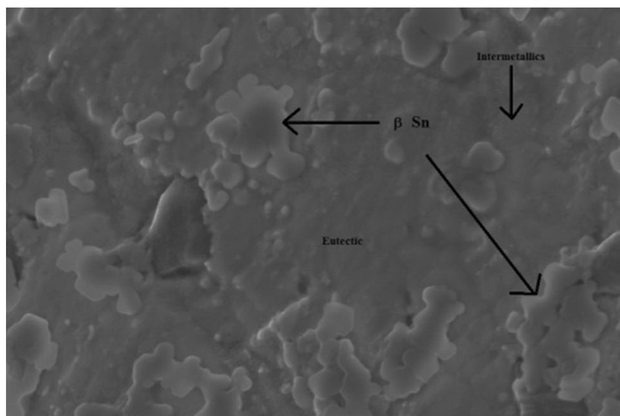


Fig. 5 FE SEM image of Sn–0.5Cu–3Bi–1Ag at 50 K

know the effect of addition of Ag into the Sn–Cu–Bi alloy. The results were noted down and the comparison is shown in Fig. 3. It can be found that the hardness value increases as the amount of Ag is increased in the Sn–Cu–Bi alloy. The hardness value of Sn–Cu–Bi alloy is found to be 19.8 Hv, and when 1% of Ag is added to this alloy, hardness value is found to be increased to 24.2 Hv (around 22%). A comparison of microhardness value of these five alloys with SAC305 and SAC405 were also conducted. The microhardness property values of SAC305 and SAC 405 were taken as 13.47 Hv and 13.98 Hv [31]. A comparison of microhardness value with Sn–0.7Cu–0.05Ni, Sn–0.7Cu–n-Ni–xTiO_2 was also done [32]. It can be analyzed that these five alloys possess higher hardness value when compared to SAC305, SAC405, Sn–0.7Cu–0.05Ni and Sn–0.7Cu–0.05Ni–xTiO_2. The presence of Ag in the solder matrix holds the grain boundaries, about to happen their sliding and allegedly strengthening the microhardness of the composite solder according to the dispersion strengthening mechanism. There is a gain in strength as the grain size decreases. In other words, the hardness of the Sn–0.5Cu–3Bi is found to be increasing with the addition of Ag.

3.5 Microstructure Evaluation

Scanning electron micrographs will give the detailed and accurate microstructure of the solder alloys. The surface details of the samples were analyzed by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Sigma). The micrographs of four alloys are shown in Fig. 4. The FE SEM image of Sn–0.5Cu–3Bi–1Ag is shown in the Fig. 5. The addition of Ag has altered the microstructure of Sn–Cu–Bi. The microstructure of Bi-containing alloys varies in terms of particles morphology, and their overall impact on the mechanical properties [30]. It can also found from the studies that addition of small amount of Bi to SAC157 alloy

can refine the needle-like Ag3Sn and Cu6Sn5 IMCs, and develop the eutectic area [30]. The microstructure analysis of alloys have as far as the knowledge the coarse β Sn grains. Ag3Sn, Cu6Sn5 and tin in the alloys are found in the eutectic region. With the addition of Ag, the β-Sn grains refine in a better way. Eutectic bands become narrower rather. Ag was uniformly distributed on the surface of the solder matrix which can be observed from the microstructure evaluation. The presence of Bi and the varying Ag particle influences the solidification process. There may be a rapid change in it. The mechanical properties are changed due to the different microstructure of the alloys, Mainly the change is size of β-Sn grains and IMC particles. Some intermetallics become coarse with the increasing of Ag content. The slipping of dislocation is prevented by the refined grain boundary and the homogeneous dispersion of Cu_6Cu_5 at the grain boundary of the β-Sn dendrites. α phase Cu and β phase Ag are also seen in the evaluation. The formation of Ag_3Sn in the matrix has altered the above properties which resulted in the decrease of melting temperature on addition of Ag incrementally. The reinforcement addition could modify the surface instability and the variation in the physical properties and the grain boundary characteristics.

4 Conclusion

The effect of Ag addition into Sn–0.5Cu–3Bi solder alloy on the microstructure and mechanical properties has been investigated. The addition of Ag resulted in decrease of melting temperature of the solder alloy on increasing concentration. The formation of Ag_3Sn in the matrix has altered the properties which resulted in the decrease of melting temperature on addition of Ag incrementally. The addition of Ag resulted in increase of the microhardness of the solder alloy. The presence of Ag in the solder matrix holds the grain boundaries, about to happen their sliding and allegedly strengthening the microhardness of the composite solder according to the dispersion strengthening mechanism. There is a gain in strength as the grain size decreases. In other words, the hardness of the Sn–0.5Cu–3Bi is found to be increasing with the addition of Ag. Contact angle is found to be decreasing with the addition of Ag. The addition of Ag can decrease surface tension of the given alloys. The improvement of the wetting behavior has been observed due to the Ag addition. The improvement on wettability of Sn–Cu–Bi solders can be examined through the outcome of adding Ag to impact the surface tension. The microstructure observations revealed that the Ag was uniformly distributed on the surface of the solder matrix. The mechanical properties are changed due to the different microstructure of the alloys; mainly the change is size of β-Sn grains and IMC particles. Some intermetallic becomes coarse with the increasing of Ag content. The reinforcement addition could modify the surface instability and the variation in the physical properties and the grain boundary characteristics.

The recommended content of the Ag to be added into the Sn–0.5Cu–3Bi solder alloy is 1.0 wt%. This alloy shows significant increase of mechanical properties and wettability. With the observed better properties it can be considered as the potential alternatives to lead–tin alloy. It can be used in the electronic packages in the automobiles where the temperature is relatively high.

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