Intermetallic formation and characterization of Sn-Cu-Mn-Ag lead-free soldering alloys

D A Padmanaban1, D A J Sunderraj2,3 and K A V Geethan2

1Department of Mechanical Engineering, SSN College of Engineering, Kallavakkam-110, India
2Department of Mechanical Engineering, St. Joseph’s College of Engineering, Chennai, India

E-mail: ananthapadmanaban2@ssn.edu.in

Abstract. Two lead-free soldering alloys, namely 87Sn-7Cu-3Mn3Ag and 87.5Sn-7.5 Cu-2.5 Mn-2.5 Ag, were prepared and the effect of Mn addition to Sn-Cu-Ag alloys was studied. The alloy was characterized using XRD, DSC, and metallurgical microscopy. Hardness of the former alloy exceeded that of the latter, due to higher intermetallic formation, according to XRD studies. The DSC curves for both alloys have melting points of 219.4 °C and 219.7 °C, with a range of melting close to 10 °C. The microstructure of both alloys contains Cu6Sn5, Ag3Sn, and MnSn2 present in dendritic Sn-rich solid solution.

1. Introduction

Lead-tin eutectics have the melting point of 183 °C, while that of SnCuAg is about 217 °C. In order to reduce the melting point further, an addition of a fourth alloying element may be favorable. Indium and Gallium are known to reduce the melting point, but both of them are costly and not easy to obtain. Manganese is cheap, and it has been used in steelmaking to remove unwanted sulfur, acting as a scavenger and it also improves the hardness of the alloy, to which it is added. Hence, Mn was used in this study for the above purposes.

SnAgCu has been found suitable to replace traditional tin-lead solder. This is mainly because of its better reliability, good creep resistance, and good thermal fatigue properties [1, 2]. Pb-Sn has a melting point of 183 °C, but Sn-Zn-Cu alloys have melting points close to 217 °C. Reflow temperature will be high if melting point is high, and this will lead to thermal damage of the polymer substrate [3]. Research on Sn-based lead free alloys has shown that under certain condition, tin whiskers are formed, which lead to short circuits and systems failures in alloys [4]. Mn and Ti have been added in trace elements, and it was found that the degree of undercooling was around 4-5 °C [5].

2. Experimental

2.1. Melting and alloy preparation

The individual elements, namely Sn, Cu, Mn, and Ag, were melted in a muffle furnace. The schematic of the furnace is shown in figure 1. It has a maximum melting capacity of 1400 °C. Temperature was raised slowly to 600 °C. The maximum temperature of 1260 °C was attained for Mn to melt.

2.2. Hardness

Microhardness tests were done at 5 different locations of the two samples, and average hardness was taken.

2.3. Differential Scanning Calorimeter

DSC was done to determine the melting points of the two alloys and also to check if there is considerable difference in melting point while changing alloy element 5% age.
2.4. X Ray studies
X-Ray diffraction peaks were obtained using X-Ray diffractometer. XRD patterns were taken for both the samples.

2.5. Microstructure
Optical micrographs were obtained to study the microstructure and correlate with the hardness. Optical micrographs also were utilized to obtain information about the type of intermetallics present.

2.6. Microscopic studies
Photographs were taken using SEM to check for the presence of Sn whiskers.

3. Results and discussion

3.1. Hardness tests and intermetallics formation

Table 1. Shows the hardness values of Both samples.

|       | 1   | 2   | 3   | 4   | 5   | 6   | Average |
|-------|-----|-----|-----|-----|-----|-----|---------|
| Sample 1 | 26.7 | 26.4 | 28.4 | 32.5 | 28.5 | 30.4 | 28.8    |
| Sample 2 | 18.1 | 19.0 | 17.8 | 18.3 | 17.8 | 15.4 | 17.7    |

Table 1 shows the hardness value of both samples. Sample 1 contains more Ag and Mn. Since Mn addition increases hardness, it is possible that high hardness in Sample 1 is due to this fact. XRD peaks shown in figure 2 are more numerous in Sample 1. Each peak is indicative of a phase. Hardness values of Sample 1 is lesser compared to Sample 2, which contains more intermetallics. This can also be identified by microscopic studies and XRD analysis. It was shown by Zhang et al. that Ytterbium reduced growth of intermetallics [7].

3.2. XRD
XRD results for both samples show their marked differences. Positions of the peaks are the same in both XRDs. There are 4 major peaks: one near 30 degrees, one near 45 degrees, one near 65 degrees, and one near 80 degrees. But it should be noted that the intensities of the peaks are significantly higher in Sample 1. This may indicate that the same types of metallic phases are present in both samples, but the amount of metal is higher in Sample 1. This inference is also supported by the fact that both Ag and Mn contents are lower in Sample 2 than in Sample 1. Ag and Mn are known to form intermetallics. Though, this is true of most of the peaks, except the 1st peak (or a small mini-series of peaks) at 2Θ angle of 30 degrees. At this angle, the peaks in Sample 2 seem to be more pronounced and higher in intensity. Peaks were...
indexed using the JCPDS Software as shown in figure 2. The XRD graph of sample 2 shown in figure 3.

![Figure 2. XRD graph of Sample 1.](image1)

![Figure 3. XRD graph of Sample 2.](image2)

It is possible that the amount of metal represented by this peak is higher in Sample 2. The contents of all other intermetallics are lower in Sample 2. XRD should be analyzed in conjunction with hardness and DSC results, in order to obtain their reasonable critical analysis. Nai et al. [8] added carbon nanotubes (CNTs) to the Sn3.5Ag0.7Cu solder alloy. Results revealed that, with the addition of CNTs, diffusion co-efficient was lower in the nanocomposite solder; thus, the growth of IMC layer was retarded. Han et al. [9] also reported a similar kind of results in Ni-CNTs on the interfacial IMC.

3.3. Microstructure

A tree-like structure of 87Sn-7Cu-3.0Mn-3Ag is indicated in figure 4. It is not observed in Sample 2 but seems to be broken in figure 5. Han et al. [10] and Yang et al. [11] explored the effect of Ni-coated carbon addition on the structure and properties of Sn3.5Ag0.7Cu nanocomposite solder. It was inferred that Ag3Sn and Cu6Sn5 were evenly found in the solder matrix. The fourth element addition (Mn, in this case) allowed to form quaternary changes in the microstructure. Some researchers deduced that intermetallics reacted with Sn, thus refining the microstructure of SnAgCu solders. Other researchers chose to add some low-solubility and diffusivity agents, such as Al2O3, TiO2, SiC, and POSS, to Sn. Until a critical value of alloy addition was reached, the required properties were improved, but after that, the saturation and even deterioration was observed.

![Figure 4. Microstructure of 87Sn-7Cu-3.0Mn.](image3)

![Figure 5. Microstructure of 87.5Sn-7.5Cu-2.5Mn-2.5Ag.](image4)

3.4. DSC results

DSC curve shows a phase change at 219.4 °C for the first sample (figure 6) and 219.7 °C for the second sample (figure 7). Melting point of Sn-Ag-Cu alloys is about 217 °C, so it appears that Mn increased the melting point. Variations in alloy elements in both samples may result in minor variations in melting
points. When 0.2% Fe was added, Sn-Ag-Cu alloys exhibited two maxima at 220 and 235 °C. When 0.6 wt.% Fe was added, only one maximum at 221.35 °C was observed, showing that it has an invariant composition [12]. The Sn-Ag-Cu equilibrium diagram [13] shows two steps in the DSC. This is possibly due to melting of invariant β-Sn + Ag3Sn+ ηCu6Sn5 phase and melting of primary β-Sn. A detailed analysis of the intermetallics formation, XRD analysis, and diffusion studies in Sn-Cu alloys have been performed by Mookam et al. [14].

![Figure 6. DSC image of Sample 1.](image)

![Figure 7. DSC image of Sample 2.](image)

3.5. SEM results

Figures 8 to 10 present the SEM images of Samples 1 and 2. No Sn whiskers, which may deteriorate the electrical properties, are observed in both alloys. Chuang and Lin [15] demonstrated that the addition of 0.5% Zn to Sn-Ag-Cu solder made the grains finer and reduced the number of such whiskers. The possibility of short circuiting due to Sn whiskers has been discussed in detail in a recent work by Karth et al. [16]. Figure 10 shows Sn whiskers in a recent research work by Arthur et al. [17]. These whiskers occur under certain manufacturing conditions that differ from alloy to alloy.
Figure 8. SEM image of Sample 1

Figure 9. SEM image of Sample 2

Figure 10. Scanning electron microscope image with Sn whiskers.

4. Conclusions
Hardness of 87.5Sn-7.5Cu-2.5Mn-2.5Ag alloy is lower than that of 87Sn-7Cu-3.0Mn-3Ag. Cu$_5$Sn$_5$, Ag$_3$Sn and MnSn$_2$ in dendritic form were found in both alloys in a Sn-rich solid solution ($\beta$ Tin). There is presence of intermetallics in both samples. DSC results show that the melting points of samples 1 and 2 were 219.4 and 219.7 °C, which suggests a marginal increase in melting point via the addition of Mn to the ternary Sn-Ag-Cu. Besides, Mn plays a major role in purifying the alloy.

Acknowledgments
The authors gratefully acknowledge the support from Management of St. Josephs Institute of Technology and SSN College of Engineering. They also thank undergraduate students Sri Bruhan and Thirumani, who helped in carrying out the experiments.

Reference

[1] Xu S, Habib A H, Pickel A D and McHenry M E 2015 Magnetic nanoparticle-based solder composites for electronic packaging applications Prog. Mater. Sci. 67 95-160
[2] Keller J, Baither D, Wilke U and Schmitz G 2011 Mechanical properties of Pb-free SnAg solder joints Acta Mater. 59 2731-41
[3] Shalaby M R 2012 Effect of silicon addition on mechanical and electrical properties of Sn-Zn based alloys rapidly quenched from melt Mat. Sci. Eng. A 550 112-7
[4] Gain A K and Chan Y C 2012 The influence of a small amount of Al and Ni nano-particles on the microstructure, kinetics and hardness of Sn-Ag-Cu solder on OSP-Cu pads Intermetallics 29 48-55
[5] Lin LW, Song J M, Lai Y S, Chiu Y T, Lee N C and Uan J Y 2009 Alloying modification of Sn-Ag-Cu solders by manganese and titanium Microelectron Reliab 49 235-41
[6] Zhang L, Fan X Y, Guo Y H and He C W 2014 Properties enhancement of SnAgCu solders containing rare earth Yb Mater. Design. 57 646-51

[7] Tay S L, Haseeb A S M A, Johan M R, Munroe P R and Quadir M Z 2013 Influence of Ni nanoparticle on thermoproperties and growth of interfacial intermetallic compounds between Sn-3.8Ag-0.7Cu lead-free solder and copper substrate Intermetallics 33 8-15

[8] Nai S M L, Wei J and Gupta M 2009 Interfacial intermetallic growth and shear strength of lead-free composite solder joints J. Alloy. Compd. 473 100-6

[9] Han Y D, Jing H Y, Nai S M L, Xu LY, Tan C M and Wei J 2012 Interfacial reaction and shear strength of Ni-coated carbon nanotubes reinforced Sn-Ag-Cu solder joints during thermal cycling Intermetallics 31 72-8

[10] Han Y D, Nai S M L, Jing H Y, Xu LY, Tan C M and Wei J 2011 Development of a Sn-Ag-Cu solder reinforced with Ni-coated carbon nanotubes J. Mater. Sci.-Mater. El. 22 315-22

[11] Yang Z B, Zhou W and Wu P 2014 Effects of Ni-coated carbon nanotubes addition on the microstructure and mechanical properties of Sn-Ag-Cu solder alloys Mat. Sci. Eng. A 590 295-300

[12] El-Daly A A, Hammad A E, Al-Ganainy G S and Ragab M 2014 Influence of Zn addition on the microstructure, melt properties and creep behavior of low Ag-content Sn-Ag-Cu lead free solder Mat. Sci. Eng. A 608 130-8

[13] Shnawah D A, Sabri M F M and Badruddin I A 2011 A review on thermal cycling and drop impact reliability of SAC solder joint in portable electronic products Microelectronics Reliability 52 90-9

[14] Mookam N, Tunthawiroon P and Kanlayasiri K 2018 Effects of copper content in Sn-based solder on the intermetallic phase formation and growth during soldering 9th Int. Conf. on Mechatronics and Manufacturing 36 1-5

[15] Chuang T H and Lin H J 2009 Inhibition of whisker growth on the surface of Sn-3Ag-0.5Cu0.5Ce solder alloyed with Zn J. Electron. Mater. 38 420-4

[16] Alagarsamy K, Kohani M, Fortier A and Pecht M G 2018 J. Biomed. Eng. Res. 2 1-5

[17] Arthur Jebastine Sunderraj D, Ananthapadmanaban D, Arun Vsanatha Geethan K and Kumar R 2019 Challenges in manufacture and use of lead free solders ISERMAT Int. Conf. (March 2019, SSN College of Engineering, Chennai, India)