IOP Conf. Series: Materials Science and Engineering **318** (2018) 012062 doi:10.1088/1757-899X/318/1/012062

The Effect of Copper Addition on the Properties of Sn-0.7Cu Solder Paste

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Abstract. The effect of copper addition on the properties of Sn-Cu based solder paste were investigate through this study. The Sn-0.7Cu solder paste doped with different concentration of Cu were prepared using solder paste mixture. The bulk solder microstructure of as-solidified solder paste was studied. Besides that, intermetallic compound (IMC) formation on Cu substrate and hardness of all solder paste also being investigated. Results shows that increasing Cu concentration cause formation of large Cu_6Sn_5 IMC at bulk solder and the size of the IMC grew larger at high temperature. In addition, β-Sn area reduce when Cu concentration was high. The IMC morphology for all solder paste almost remain unchanged. However, there are large Cu_6Sn_5 IMC form near the interfacial IMC in Sn-Cu solder paste with high amount of Cu (Sn-10Cu). The hardness value was decrease when processing temperature at 250 °C due to present of small void in the microstructure while hardness of solder material increased at high temperature.

1. Introduction

Soldering technology plays an important role in electronic industry since it provided a metallurgical bonding between electronic component and substrate [1]. Lead (Pb) free solder has been highly demanded for usage in electronics packaging and assembly as a replacement for leaded solder [2]. The usage of leaded solder in electronic industry has been banned because of its toxicity that can harmful to individual health and also environment [3]. Since then, several studied have been made to developed new Pb free solder for replacing the existing Pb solder [4-8]. Nowadays, Sn-Ag-Cu based solder alloy was recognize as candidates for replacing Pb solder due to their good properties [9, 10]. On the other hand, less effort has been given to the development of much cheaper Sn-Cu solder alloys [11]. The properties of Sn-Cu solder could might be improve through micro-alloying [12] by addition of minor elements such as nickel [11, 13].

During liquid-solid reaction, solder paste will melt and wet the Cu substrate and hence resulting in the formation of intermetallic compound (IMC) layer. This IMC not only provide the joining but also the electrical and mechanical continuity in electronic assemblies. However, excessive IMC layer thickness prone to has deteriorate effect on solder properties due to high brittleness of the IMC [14]. Therefore, IMC formation of the solder joint in electronics packages become critical concern in the microelectronics industry [4, 15]. Basically, IMC that form from reaction between Sn-based solder with Cu substrate is scallop morphology of the Cu_6Sn_5 and Cu_3Sn when subjected to extensive soldering time or high temperature.

In this study, the main objectives are to investigate the effect of Cu addition in Sn-0.7Cu solder paste on the properties such as bulk microstructure, morphology of IMC layer and hardness during liquid solder/solid Cu substrate reaction for different soldering (processing) temperature.

2. Experimental procedure

Sn-0.7wt. % Cu solder paste (supplied by Nihon Superior Co. Ltd, Japan) was used as based material to produce new solder paste (Sn-4 wt. % Cu and Sn-10 wt. % Cu). The new solder pastes were prepared by mechanically mixing Sn-0.7wt. % Cu solder paste with copper particle using solder paste mixer. The mixing process was carried out for approximately 30 minutes to achieve homogeneity. To produce a solder joint, about 0.1 g of solder paste was then deposited on copper substrate and melted in furnace for temperature about 250 °C and soak for 2 minute. Besides that, solder paste also was place into crucible and melt for different temperature (250 and 500 °C).

The sample was then mounted using epoxy resin before metallography sample preparation (grinding, polishing and etching). The bulk microstructure and interfacial intermetallic compound (IMC) layer was observed under Optical Microscope (OM) and Scanning Electron Microscope (SEM). The mechanical properties of bulk solder was evaluated through vickers microhardness tester. The microhardness of the bulk solder alloy were tested using Micro Vickers testing machine with load of 9.81 N and dwell time of 10 s for each indentation. There are 15 indents were taken for each sample and the average value for the hardness value was then calculated.

3. Results and discussion

3.1. Bulk microstructure

Figure 1 show the optical microscope images of the Sn-Cu bulk solder microstructure with different Cu composition and also processing temperature. Two visible region of β-Sn phase and Sn-Cu eutectic phase of Cu_6Sn_5 can be observed on the microstructure of the solder paste. Generally, the microstructure of the Sn-0.7Cu solder after solidified consists of β-Sn phases (light colour), and SnCu phase which usually consist of needle-like Cu_6Sn_5 IMCs, eutectic Sn-Cu area [16].

Accordingly, it can be seen that there are changes in the bulk solder microstructures where the composition of Cu is different and the processing temperature varies. As can be seen in Figure 1(c and e), increasing amount of Cu reduce β-Sn area. Other than that, higher processing temperature results in larger grain size while lower temperature results in smaller grain size. In addition, Cu_3Sn IMC surrounded with Cu_6Sn_5 IMC was clearly observed at samples with high Cu concentration (Sn-10Cu).

Figure 2 shows the SEM image of Sn-4Cu solder after solidified. From the SEM/EDX analysis, it was clearly observed that the light area was β-Sn phase while the large particle is Sn-Cu eutectic phase of Cu_6Sn_5. Hung et al. [17] states that the amount of Cu composition in Sn-Cu solders influences the Cu-Sn intermetallic formation where increasing the Cu content increases the Cu-Sn intermetallic and decreases the area of the Sn-rich phase. According to Shen et al. [18] Cu has ability to refine the grain size of Bi-rich phase solder as Cu reacts with Sn to form Cu_6Sn_5 IMC particles and act as heterogeneous nucleation sites during solidification process.

Previous studies reported that adding some elements into solder alloy may alter the microstructure and thus improved the properties [19]. Zheng et al. reported that through microalloying, the microstructure of Sn-0.7Cu added with Ni and Zn were alter and a fully eutectic was obtained. Other than that, Nogita et al. found that Ni additions dramatically alter the nucleation patterns and solidification behaviour of the Sn–Cu_6Sn_5 eutectic in Sn-0.7Cu solder [20].

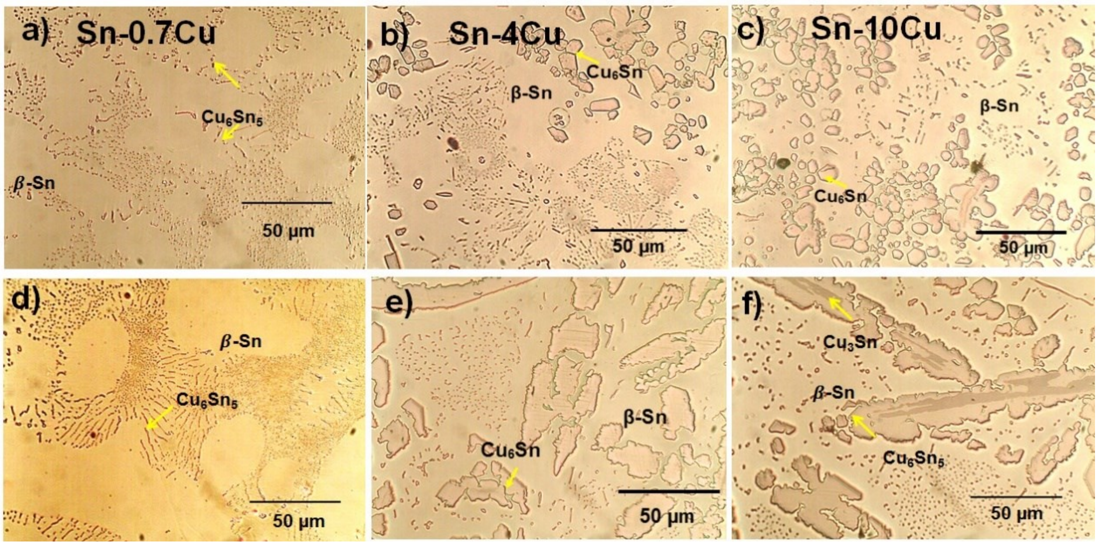

Figure 1. Bulk microstructure of as-solidified at 250 °C (a-c) and 500 °C (d-e) processing temperature.

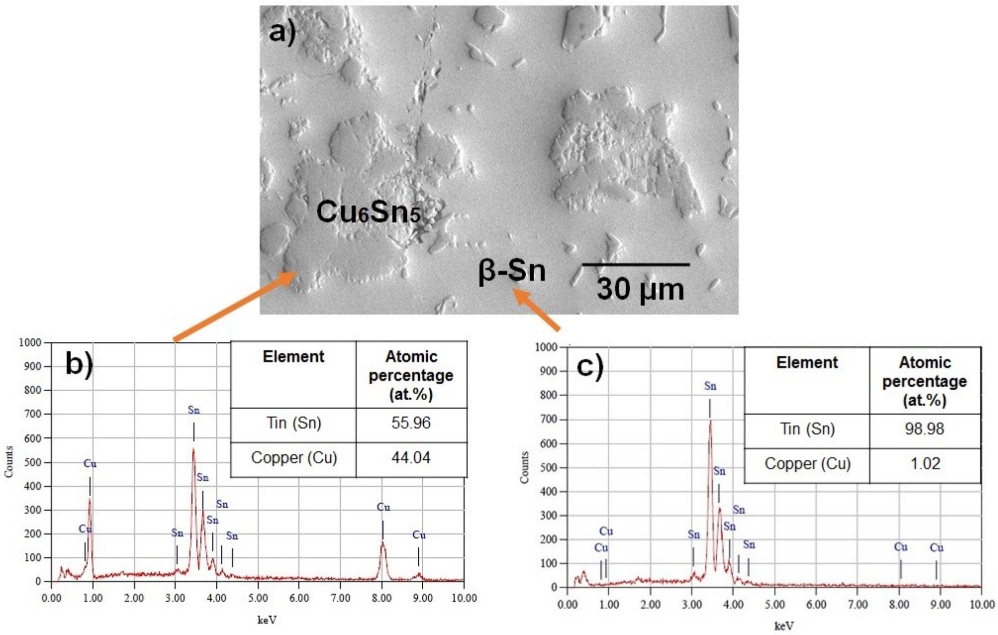

Figure 2. SEM/EDX Micrographs (a) bulk microstructure of Sn-4Cu, (b) Cu_6Sn_6 and (c) Tin (Sn) element detected.

3.2. Intermetallic compound formation

Figure 3 depict the SEM morphology of intermetallic compound (IMC) for Sn-Cu solder paste on Cu substrate. The scallop-type morphology was observed in all solder joints. Increasing amount of Cu into solder paste unchanged the morphology of the solder joint. In contrast, the formation of Cu_6Sn_5 IMC near the interfacial IMC results in larger size for solder paste with high Cu concentration (Figure 3c).

During soldering, solder paste will melt and wet Cu substrate resulting in the formation of IMC layer along the substrate. The diffusion of Cu atom from the Cu substrate and Sn atom from solder to the interface between melt solder and substrate will continue until Sn become supersaturated. Clearly, the Cu_6Sn_5 IMC was first precipitated from the supersaturated Sn liquid phase. Scanning Electron Microscope equip with Energy-Dispersive X-ray (SEM/EDX) result in Fig. 4 shows the IMC phase that form during early soldering was considered to be Cu_6Sn_5 by referring to the atomic ratio of Cu and Sn nearly to 6:5.

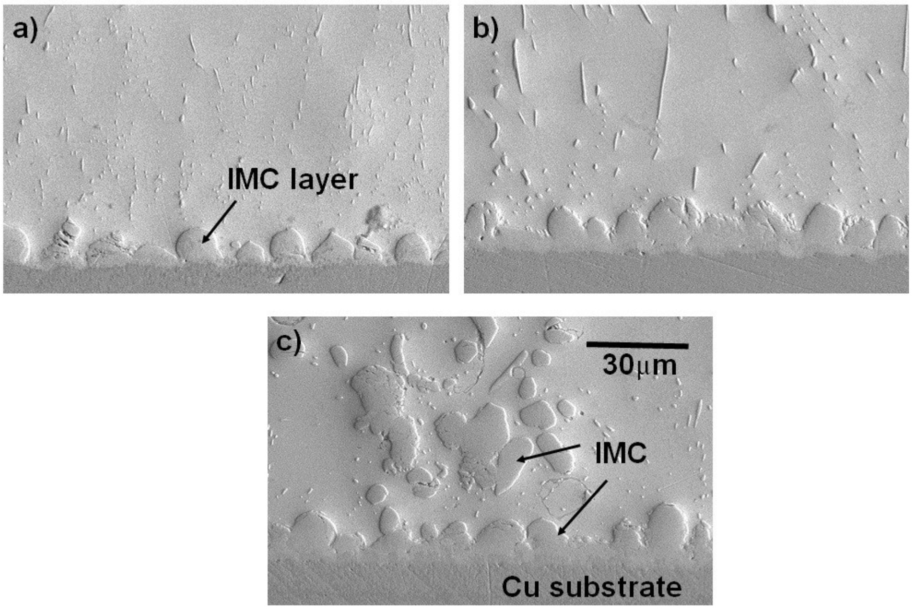

Figure 3. SEM image of intermetallic compound formation at 250 °C; (a) Sn-0.7Cu, (b) Sn-4Cu and (c) Sn-10Cu.

Cu_6Sn_5 IMCs are formed first because a large driving force for the metallurgical reaction between copper (Cu) and tin (Sn) atoms exists at the metastable composition. Scallop-type Cu_6Sn_5 first formed at the Sn/Cu interface during soldering, and its rate of formation is very fast. Cu_6Sn_5 was formed by the dissolution of Cu, followed by a metallurgical reaction. If contact with the molten solder is long enough, Cu_3Sn IMC formed between Cu_6Sn_5 and Cu. Cu_3Sn was formed by diffusion and by reaction type growth [21].

Formation of large Cu_6Sn_5 near the interfacial Cu_6Sn_5 IMC of Sn-10Cu might due to the high amount of Cu supplied in the solder compare to low Cu concentration of solder paste (Sn-0.7Cu and Sn-4Cu). Hence, this situation cause the formation of many Cu_6Sn_5 IMC located at near interfacial IMC also at bulk solder (Figure 1e).

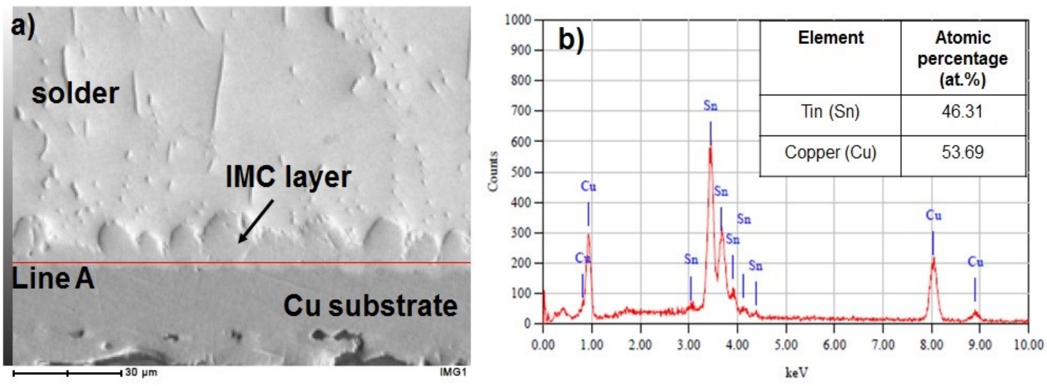

Figure 4. Line analysis of Sn-0.7Cu on Cu substrate.

3.3. Hardness

Figure 5 shows the bar chart for micro hardness value for Sn-Cu solder alloy with varying in Cu concentration at different processing temperature. Based on the bar chart (Figure 5a), the microhardness value of bulk solder alloys that melted at 250 ℃ has decreasing pattern as Cu composition in the solder alloys was increased.

Meanwhile, the value of microhardness for solder alloys melted at 500 °C were increased as the Cu composition in solder alloy increased as shown in Figure 5b. Rehim and Zahran have reported in their research that the increasing in microhardness is might be due to the presence of denser, harder and stiffer η-phase and ε-phase IMCs. This IMC act as a barrier for localized plastic deformation of the Sn-matrix during localized indentation (microhardness testing). The value of microhardness of the solder also may be affected by the microsturucture of the solder that is formed after solidified [11].

As for the solders melted at 250 °C, increasing Cu composition containing elevated number of porosity present in the bulk solder. Thus, this situation can lower hardness value of Sn-10%Cu. The mechanical properties always related to the microstructure of solder joint in which become very important to ensure prolong reliability during service.

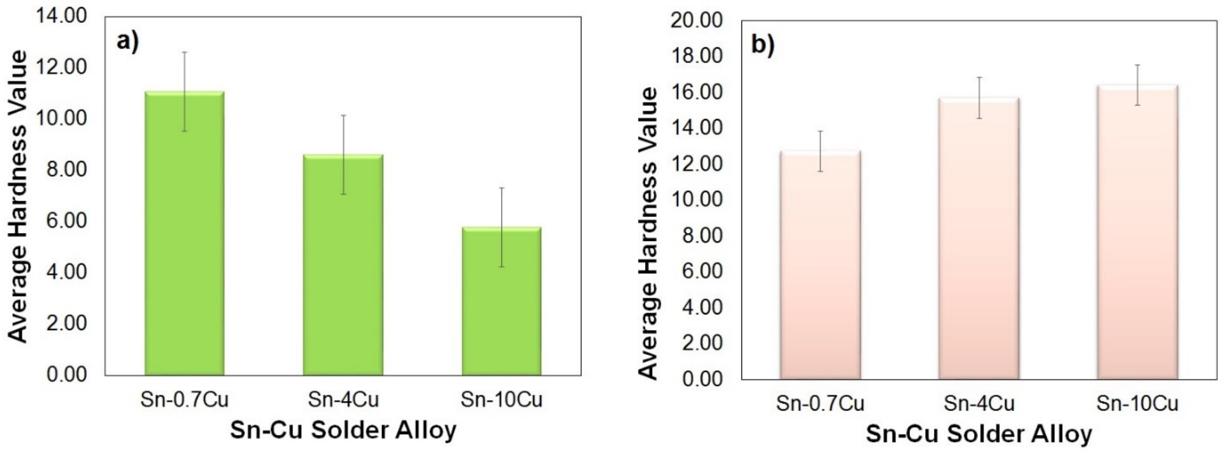

Figure 5. Microhardness value fo Sn-Cu solder alloys melted at (a) 250 °C and (b) 500 °C.

4. Conclusion

The effect of Cu addition on the microstructural and mechanical properties for Sn-Cu solder was examined through this project. These solder alloys were compared based on their properties after being melted in temperature of 250 °C and 500 °C with Cu composition of 0.7wt% Cu, 4wt%Cu and 10wt%Cu. The conclusions that can be drawn from this research are:

a) The microstructure and the morphology for bulk solder alloys were changed due to addition of Cu and increasing processing temperature. The size of Cu_6Sn_5 grains increases at higher Cu composition and higher melting temperature. Besides that, β-Sn area was reduce at higher Cu composition in bulk solder alloys.
b) As the Cu concentration increase, the Cu_6Sn_5 IMC grew larger near the interfacial IMC. Unfortunately, the interfacial IMC remain unchanged.
c) The solder paste that melted at 250 °C and solder with 10 % of Cu has the lowest hardness value compared to other two compositions. While for solder melted in 500 °C, pure Sn-0.7Cu solder has the lowest hardness value compared to other two compositions.

Acknowledgement
The authors gratefully acknowledge Nihon Superior Co. Ltd, Japan for supporting the research effort through materials.

References
[1] Musa S A, Mohd Salleh M A A and Saud N 2013 *Adv. Mater. Res.* **795** 518-521
[2] Mohd Salleh M A A, M.H.Z. Hazizi, Z.A. Ahmad, K. Hussin, and K.R. Ahmad 2011 *Adv. Mater. Res.*
[3] Mohd Salleh M A A, McDonalda S D, Terada Y, Yasuda H, and Nogita K 2015 *Mater. Des.* **82** 136–147
[4] Mohd Salleh M A A, McDonald S D, Gourlay C M, Yasuda H, and Nogita K 2016, Mater. Des. **108** 418–428
[5] Zhao Z, Liu L, Choi H S, Cai J, Wang Q, Wang Y, and Zou G 2016 *Microelectron. Relia.* **60** 126-134
[6] Zhao X, Wen Y, Li Y, Liu Y, and Wang Y 2016 *J. Alloys Compd.* **662** 272-282
[7] Mohd Salleh M A A, McDonald S D, and Nogita K 2013 *Appl. Mech. Mater.* 260-6
[8] Somidin F, Mohd Salleh M A A, and Ahmad K R 2013 *Adv. Mater. Res.* **620** 105-111
[9] Yahaya M Z, Ani F C, Samsudin Z, Sahin S, Abdullah MZ, and Mohamada A A 2016 *Mater. Sci. Eng., A* **669** 178–186
[10] Sun L and Zhang L 2015 *Adv. Mater. Sci. Eng.* 16
[11] Harcuba P and Janeček M 2008, *WDS'08 Proceedings of Contributed Papers* 220–224
[12] Zeng G, McDonald S D, Mu D, Terada Y, Yasuda H, Gu Q, Mohd Salleh M A A, and Nogita K 2016 *J. Alloys Compd.* **685** 471-482
[13] Mohd Salleh M A A, McDonald S D, Gourlay C M, Belyakov S A, Yasuda H, and Nogita K 2016 *J. Electron. Mater.* **45**(1)
[14] Ramli M I I, Saud N, Mohd Salleh M A A, Derman M N, and Said R M 2016 *Microelectron. Relia.* **65** 255–264
[15] Mohd Salleh M A A, McDonald S D, and Nogita K 2017 *Mater. Process. Technol.* **242** 235-245
[16] Abd El-Rehim A F and Zahran H Y 2017 *J. Alloys Compd.* **695** 3666-3673
[17] Hung F Y, T S Lui, Chen L H, and He N T 2008 *J. Alloys Compd.* **457**(1) 171-176
[18] Shen J, Pu Y, Yin H, Luo D, and Chen J 2014 *J. Alloys Compd.* **614** 63-70
[19] Zeng G, McDonald SD, Gu Q, Terada Y, Uesugi K, Yasudad H and Nogita K 2015 *Acta Mater.* **83** 2419-25
[20] Nogita K, Read J, Nishimura T, Sweatman K, Suenaga S and Dahle AK 2005 *Mater. Trans*. **46** 2419-25
[21] Lee LM and Mohamad AA 2013 *Adv. Mater. Sci. Eng*.