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Effect of Alloying Element on Microstructure and Mechanical Properties of Sn-0.7cu Solder

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ABSTRACT. Due to environment concern of lead Sn-0.7Cu eutectic solder has been successfully applied to practical production of consumer products. However, Sn-Cu has been reported to exhibit somewhat inferior mechanical properties compared to Ag containing lead free solder alloys. In this work, 1.0wt.% In and 0.1wt.% Fe had been added into Sn-0.7Cu eutectic solder. Three different solders have been fabricated by adding In and Fe into the solder, i.e., Sn.0.7Cu, Sn.0.7Cu.1.0In and Sn.0.7Cu.1.0In.0.1Fe. DSC result showed that adding indium decreases the melting point of Sn-Cu solder. The addition of In and Fe is expected to refine the β-Sn grains with fine Cu_6Sn_5 distributed within the eutectic colony of the bulk solder and contribute to higher solder strength. Characterization of the solder alloys focused on the bulk solder microstructure, IMC evaluation and wettability of solder alloys in reflowed and aged conditions. Reflow temperature was 270°C. Aging was done for 100, 250 and 500 hours at 150 °C and 180°C. The IMC observed for reflowed samples seem to decrease in thickness with addition of In and Fe. Isothermally aged samples on the other hand, did grow at higher rate when In and Fe was added. The IMC formed at the interface between solder and the copper substrate was identified as Cu_6Sn_5in reflowed samples, and both $Cu_6Sn_5$and Cu_3Sn when aged. The shear strength of samples improved as In and Fe were added.

***Keywords**: Lead-free solder, Sn-Cu alloy, Isothermal aging, Microstructure, Intermetallic compound;*

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1. INTRODUCTION

The soldering process has been a fundamental aspect in the realisation of all electronic products since the commencement of the electronic age and has been used extensively in the electronic industry. Due to environmental issue over the toxicity of lead (Pb) in eutectic Sn-Pb solders, has induce the development of lead free solder alloys for electronic packaging [1]. Sn-Pb solder have been long considered as the most common material for electronic packaging, since they have low melting point, low cost and good wettability [2]. There are several lead-free solders develop for better mechanical and electrical properties including Sn-Ag, Sn-Cu, Sn-Zn and Sn-Ag-Cu. Among these alloys Sn-Cu binary alloy, shows most suitable as a low-cost substitute lead-free solder alloy to replace Sn-Pb solder alloy, especially for iron, dip and wave soldering operation [3]. As the addition other alloying element such Zn, In, Fe, Bi can give good properties for solder that will give lower wetting angle, good spreading, lower melting point, smaller grain and others. In this work, 1.0wt.% In and 0.1wt.% Fe had been added into Sn-0.7Cu solder. Addition of In and Fe haves how improved in joint embrittlement, wet ability, lower the melting range and improved shear strength and increasing the fracture toughness this due to better adhesion of solder with substrate and improved interface bonding [4].

The properties of solders include structure of the intermetallic compounds (IMCs), the morphology and thickness, adhesion between the IMC layer and solder, microstructure evaluation after reflow and diffusion properties [5]. The thicker of IMC layer is a sign of good wetting but its excessive growth has a detrimental effect to the reliability of the solder joint since IMC is very brittle in nature. Additions of small amount alloying elements have been reported to help reducing the thickness of the interfacial IMC layer [6,7]. It also been reported that the thickness of Cu_6Sn_5 and Cu_3Sn IMC layers increased linearly with the cube root of reflow time [8].

2. MATERIALS AND METHODS

The alloys investigated had a composition ofSn-0.7wt.%Cu, Sn-0.7Cu-1.0wt.%In and Sn-0.7wt.%Cu-1.0wt.%In-0.1wt.%Fe.They were prepared from high purity (99.998%) Sn ingot, Cu shots, In shots and Fe beads as raw material via casting. For bulk solder sample preparation, the solder alloys were ground with SiC abrasive paper grit 100 until 2000 before polished using 1 µm alumina powder. Once mirror-like surface was obtained, the samples were chemically etched with 5% HNO_3-2% HCl-93% CH_4O etching solution to reveal the microstructure before observed using field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray(EDX). The wettability of the solder was determined using a solder checker model SAT-5100 from Rhesca Co. Ltd. The temperature was set to be 270 °C with 2 mm immersing depth and 10 s immersing time. Maximum wetting force and wetting time were obtained from the wetting balance curve that was plotted automatically by the embedded software.

To make solder joint, small piece of the solder alloys was cold roll to form solder sheet with a thickness of 0.5 mm. The solder sheet was punched to form a solder disk with a diameter of 6 mm. Dimensions of 0.5 × 10 × 10 mm Cu substrate was applied with activated rosin (RA) flux to remove contaminants prior to reflow. Reflow process was done inside a reflow oven with the reflow temperature set at 270 °C. Reflowed solders were then isothermally aged at 100 °C and 150 °C for 100 hours, 200 hours and 500 hours, respectively. Subsequently, reflowed and isothermally aged solders were cut to reveal the cross section of the joint before mounted into epoxy resin. Wetting angle was measured after grinding and polishing process while IMC analysis via FESEM was done after the joint was chemically etched with the same solution as mentioned above. The grain size and the IMC thickness were measured using i-Solution DT image analyzer software.

3. RESULTS AND DISCUSSION

3.1 Differential Scanning Calorimetry (DSC). The result of DSC measurement is summarized in Table 1.The melting temperature of Sn-0.7Cu-1.0In-0.1Fe solder was found235.25°C which is significantly higher compared to other solder alloys. This due to melting point of pure Fe is much higher than Sn [5]. The decrease in the melting point of Sn-0.7Cu-1.0In solder alloy may due to the addition of low melting temperature element, such as In (T_m=157°C) [9].

Table 1 Melting temperature of solder alloy samples

Sample	Melting temperature, °C
Sn-0.7Cu	233.73
Sn-0.7Cu-1.0In	231.78
Sn-0.7Cu-1.0In-0.1Fe	235.25

3.2 Microstructure of bulk solder. The microstructure of a) Sn-0.7Cu, b) Sn-0.7Cu-1.0In and c) Sn-0.7Cu-1.0In-0.1Fe bulk solder alloys are present in Fig 1.From Fig. 1, the addition of In and Fe in

solder alloys can markedly refinement β-Sn andintermetallic compounds are more uniformly distributed. Based on EDX analysis as shown in Table 2. From the analysis, there is no formation of $InSn_4$ IMCs, although 1.0wt.% of In was added. In is only spotted near the β-Sn phase where it adhered next to the Sn of the solder alloy. According to previous work being done by other researchers, $InSn_4$ IMCs only form when 2wt.% and

4wt.% of In was added into solder sample [10,11]. In also has maximum solubility inside Sn, it would suggest that In is distributed within β-Sn phase and not formed into In_4Sn IMC [12]. Therefore, in this work, the In added could be too low for $InSn_4$ to form.

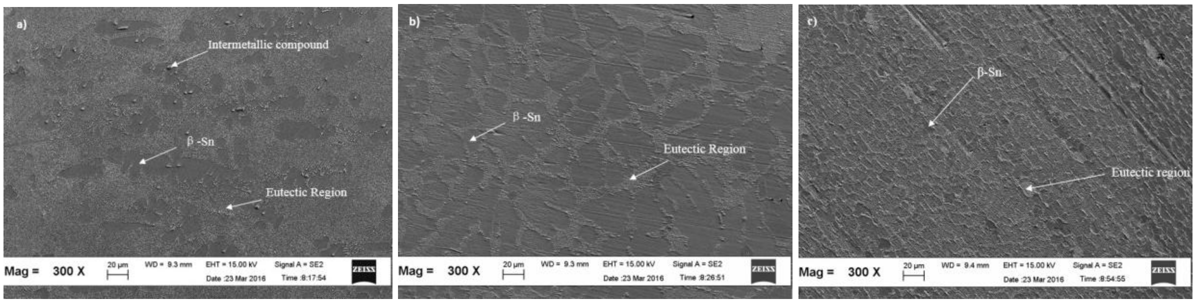

Fig. 1FESEM micrographs of (a) Sn-0.7Cu, (b) Sn-0.7Cu-1.0In and (c) Sn-0.7Cu-1.0In-0.1Fe bulk solder alloys

Table 2 Chemical composition of IMCs (At.%)

Composition	IMC	Cu	Sn	In	Fe
Sn-0.7Cu	Cu_6Sn_5	55.80	40.20	-	-
Sn-0.7Cu-1.0In	Cu_6Sn_5	58.33	41.67	-	-
	$InSn_4$	4.29	94.16	1.55	-
Sn-0.7Cu-1.0In-0.1Fe	Cu_6Sn_5	58.33	41.67	-	-
	$FeSn_2$	-	69.14	1.55	30.86

3.3 Microstructure of IMCs layer. The average thickness of IMC formed on each sample before and after aging are listed in Table 3. From the overall view on the IMC thickness, Sn-0.7Cu-1.0In solder samples have lowest IMC thickness compared to other two samples due to In hindered the dissolution of Cu to liquid solder [5,13], followed by Sn-0.7Cu and Sn-0.7Cu-1.0In-0.1Fe solder samples, this may be due to the formation of elongated scallops of Cu_6Sn_5 IMC [5].

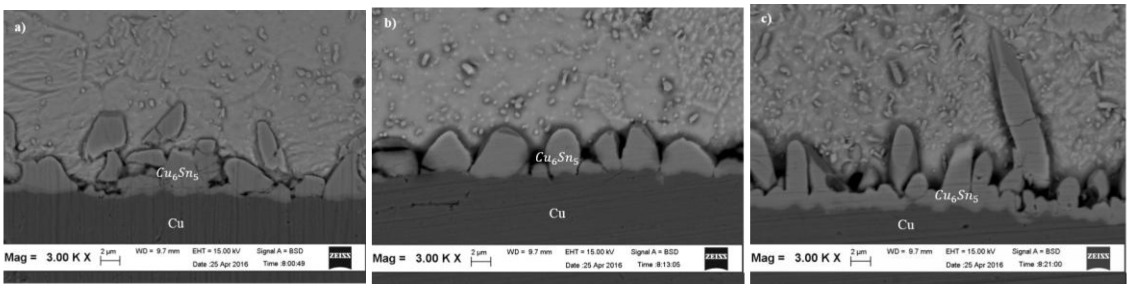

Fig. 2 Microstructure of IMC layer at solder-substrate interface for as reflowed condition (a)Sn-0.7Cu, (b) Sn-0.7Cu -1.0In and (c) Sn-0.7Cu -1.0In-0.1Fe solder alloys

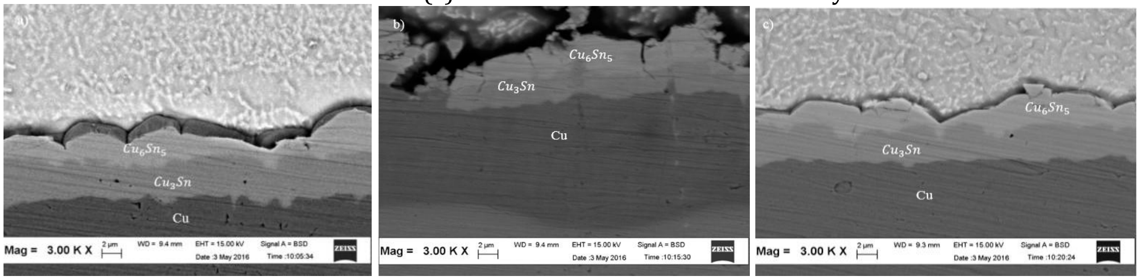

Fig. 3 Microstructure of IMC layer at solder-substrate interface after isothermally aged for 250 hours at 150 °C (a)Sn-0.7Cu, (b) Sn-0.7Cu -1.0In and (c) Sn-0.7Cu -1.0In-0.1Fe solder alloys

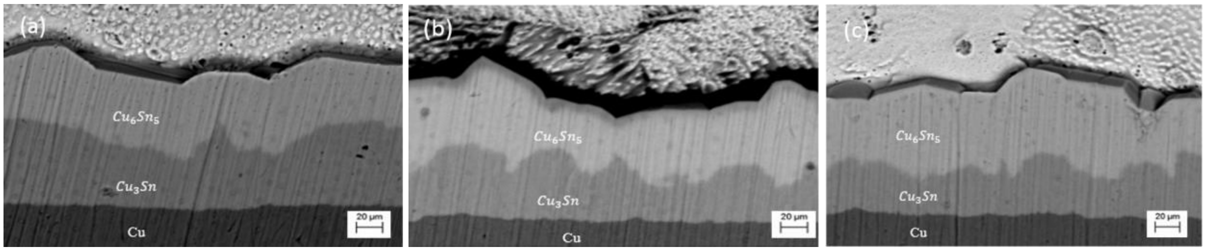

Fig. 4 Microstructure of IMC layer at solder-substrate interface after isothermally aged for 250 hours at 180 °C (a)Sn-0.7Cu, (b) Sn-0.7Cu -1.0In and (c) Sn-0.7Cu-1.0In-0.1Fe solder alloys

The average thickness of IMC formed on each sample before and after aging are listed in Table 3 and Table 4. From the overall view on the IMC thickness, Sn-0.7Cu-1.0In solder samples have lowest IMC thickness compared to other two samples, followed by Sn-0.7Cu and Sn-0.7Cu-1.0In-0.1Fe solder samples. The low overall thickness of Sn-0.7Cu-1.0In samples may due to addition of 1.0wt.% of In hindered the dissolution of Cu to liquid solder and thus reduced the thickness of the Cu_6Sn_5IMC layer compared to Sn-0.7Cu sample [5,13]. The high overall IMC thickness in Sn-0.7Cu-1.0In-0.1Fe sample may be due to the formation of elongated scallops of Cu_6Sn_5IMC [5].

The aging temperature and duration significantly increased the IMC thickness in solder samples because during aging, excess Cu will diffuse and reacts with existing intermetallic compounds and increases the size of nuclei. As results, the thickness of IMC layer increased [5,14].

Table 3 Average thickness and growth rate constant of IMC 150°Cat different aging condition

	IMC thickness (µm)					
Condition	Sn-0.7Cu	Growth rate (cm^2/s)	Sn-0.7Cu-1.0In	Growth rate (cm^2/s)	Sn-0.7Cu-1.0In-0.1Fe	Growth rate (cm^2/s)
As reflowed	3.61	0	3.53	0	3.77	0
100 h 150 °C	4.76	$3.67x10^{-14}$	4.18	$1.17x10^{-14}$	5.85	$1.2x10^{-13}$
250 h 150 °C	6.75	$1.96x10^{-13}$	6.04	$7.00x10^{-14}$	6.09	$5.98x10^{-14}$
500 h 150 °C	7.04	$6.53x10^{-14}$	6.38	$4.51x10^{-14}$	7.56	$7.98x10^{-14}$

Table 6 Average thickness and growth rate constant of IMC 180°C at different aging condition

	IMC thickness (µm)					
Condition	Sn-0.7Cu	Growth rate (cm^2/s)	Sn-0.7Cu-1.0In	Growth rate (cm^2/s)	Sn-0.7Cu-1.0In-0.1Fe	Growth rate (cm^2/s)
As reflowed	3.61	0	3.53	0	3.77	0
100 h 180 °C	8.07	$5.53x10^{-13}$	6.21	$1.99x10^{-13}$	8.33	$5.7 x10^{-13}$
250 h 180 °C	11.25	$6.49x10^{-13}$	9.34	$3.75x10^{-13}$	12.16	$7.82x10^{-13}$
500 h 180 °C	13.63	$5.58x10^{-13}$	12.42	$4.39x10^{-13}$	12.67	$4.40x10^{-13}$

3.4 Single Lap Joint. In this testing, Sn-0.7Cu-1.0In-0.1Fe gave the highest shear strength, but from the stress strain curve shown Fig.5 and summarize in Table 7, this samples exhibited lesser plastic deformation if compared to Sn-0.7Cu-1.0In solder alloy. The lesser plastic deformation is due to the addition of 0.1wt.% of Fe that caused the abnormal growth of IMCs at the interface of Cu substrate. The abnormal growth may due to the increase in the chemical activity of Cu element with the solder. This elongated IMC led to the lower fracture strain in Sn-0.7Cu-1.0In-0.1Fe solder alloy due to the IMC embrittlement [13].

Table 7 Average shear strength of solder samples

Sample	Load, N	Area, $\times 10^{-5} m^2$	Shear Strength, MPa
Sn-0.7Cu	2385.04	9.88	24.15
Sn-0.7Cu-1.0In	2479.07	9.61	25.80
Sn-0.7Cu-1.0In-0.1Fe	2541.20	9.80	25.93

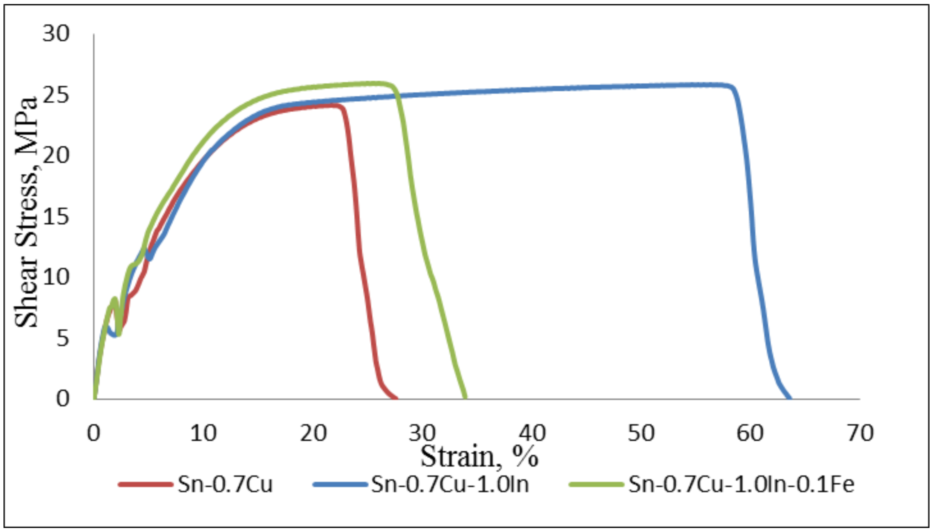

Fig. 5 Stress strain curve of solder samples

4. SUMMARY

This study found that addition of In had lowered the melting temperature of Sn-0.7Cu. In contrast, addition of Fe led to an increased in melting temperature. From the FESEM and EDX analysis, it shows that the grain size decreases as addition of In and Fe on microstructure of solder. The shear strength of samples improved as In and Fe added. From FESEM and EDX analysis, aging had led to the formation and growth of Cu_6Sn_5 and Cu_3Sn IMC, and this had increase the thickness of IMC layer.

REFERENCES

[1] A.A.E. Daly,A.Z. Mohamad, A.Fawzy,A.M.E. Taher, Creep behavior of near-peritectic Sn-5Sb solders containing small amount of Ag and Cu,Mat. Sci. Eng. A, 528 (2011)1055-1062.

[2] C.P.Lin, C.M.Chen, Y.W.Yen, H.J.Wu, S.W.Chen, Interfacial reaction between high-Pb solder and Ag,J. Alloy Compd.,509(2011)3509-3514.

[3] Z.B. Luo, J. Zhao, Y.J. Gao, L. Wang, Revisiting mechanisms to inhibit Ag 3 Sn plates in Sn-Ag-Cu solders with 1wt.% Zn addition,J. Alloy Compd., 500(2010)39-45.

[4] H.Fallahi, M. S.Nurulakmal, A. Fallahi,J.Abdullah, Modifying the mechanical properties of lead-free solder by adding iron and indium and using a lap joint test,J. Mater. Sci-Mater. El., 23 (2012) 1739-1749.

[5] H.Fallahi, M.S.Nurulakmal, F.Arezodarb,J. Abdullah. Effect of iron and indium on IMC formation and mechanical properties of lead-free solder,Mat. Sci. Eng., 553 (2012) 22-31.

[6] A.M. Yu, M.S. Kim, C.W. Lee, J.H. Lee, Wetting and interfacial reaction characteristics of Sn-1.2Ag-0.5Cu-xIn quaternary solder alloys, Met. Mater. Int., 17 (2011) 521-526.

[7] L. Gao, S. Xue, L. Zhang, Z. Sheng, F. Ji, W. Dai, Effect of alloying elements on properties and microstructures of SnAgCu solders, Microelectron., Eng. 87 (2010) 2025-2034.

[8] B.I. Noh,J.M. Koo, D.G.Kim, J.D. Nam,J. Joo, S.B.Jung, Effect of number of reflow on the mechanical and electrical properties of BGA package,Mat. Sci. Eng., 14 (2006) 1375-1378.

[9] R.M.Shalaby, Indium, chromium and nickel-modified eutectic Sn-0.7wt.%Cu lead-free solder rapidly solidified from molten state, J. Mater. Sci-Mater. El., 26 (2015), 6625-6632.

[10] A.A.E. Daly,A.E.Hammad, Enhancement of creep resistance and thermal behavior of eutectic Sn–Cu lead-free solder alloy by Ag and in-additions,Mater. Design, 40 (2012) 292-298.

[11] P.Seboa, Z.Moserb, P.Svecc, D.Janickovi,E.Dobrockad, W.Gasiorb, J.Pstrus. Effect of indium on the microstructure of the interface between $Sn_{3.13}Ag_{0.74}Cuin$ solder and Cu substrate,J. Alloy Compd., 480(2009) 409-415.

[12] Rodrigues, F. et al., (2017). Study of intermetallic compounds (IMC) that form between indium-enriched SAC solder alloys and copper substrate. , pp.603–611

[13] T. Laurila,V. Vuorinen, M.P.Krockel, Impurity and alloying effects on interfacial reaction layers in Pb-free soldering,Mat. Sci. Eng.,68 (2010) 1-38.

[14] M.J. Rizvi, C. Bailey,Y.C.Chan, M.N.Islam, H.Lu, Effect of adding 0.3wt.% Ni into the Sn-0.7wt.%Cu solder:part II. Growth of intermetallic layer with Cu during wetting and aging,J. Alloy Compd., 438(2007) 122-128.