The Sn-3.5Ag-1.0Cu-0.1Zn/Cu Intermetallic Interface under Thermal Aging

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Abstract

Due to environmental concerns, lead-free solders were introduced to replace the lead-based solders in microelectronics devices technology. Although there were many lead-free solder available, the Sn-Ag-Cu was considered as the best choice. But the solder has its draw backs in terms of melting temperature and intermetallic formations. To improve the solder, a fourth element Zn was added into the solder and was synthesized via powder metallurgy route. This research studies the effect of 0.1wt% Zn addition on the mechanical properties and intermetallic formation on Cu substrate. For the mechanical test, the Vickers hardness (Hv), yield strength (σ_y) and ultimate tensile strength (σ_{UTS}) were reported. The mechanical test for Zn based composites solder shows better properties compared to un-doped counterparts. For intermetallic, the solders were melted at 250°C and aged at 150°C until 400 hours. The phases formed and its growth was studied under SEM and by energy dispersive x-ray (EDX). The addition of Zinc has improved the mechanical properties of Sn-Ag-Cu solder, while the SEM results show the presence of Cu_6Sn_5 and Cu_3Sn intermetallics. The addition of 0.1wt% Zn has retarded the growth of the Cu3Sn intermetallic but not the total intermetallic thickness.

Keywords: Sn-Ag-Cu-Zn Solder, Intermetallic, Mechanical Properties and Powder Metallurgy

Introduction

Previously, the solder interconnection was made from the Sn–Pb alloys which offer good combination of low cost, low melting temperature, good mechanical properties and excellent wetting properties on substrates. However, in view of the toxicity of Pb, Pb-based alloys present potential healthy and environmental concerns, and has been comprehensively prohibited and thus the development of lead-free solders with at least same microstructure stability and mechanical properties as eutectic Sn-Pb solder is in progress (Song et al., 2010 and Yu et al., 2004).

Among the tin-based lead-free solder alloys, the ternary Sn-Ag-Cu solder alloy has been recommended as substitutes for Sn-Pb eutectic solder. Unfortunately, the solder system has high melting point compared to Sn-Pb solder. The minor addition of Zn is believed to lower down the melting temperature, enhance the mechanical properties and also refines the solder microstructure of the Sn-Ag-Cu alloy.

During soldering in electronic interconnections, the formation of intermetallic compounds (IMCs) at solder/substrate interface is inevitable for the joining action. However, during storage and field service, the growth of IMCs will influence the strength of solder joints and result in mechanical failure of the joints. Therefore, the formation and growth of IMCs during soldering and long-term thermal aging has been widely studied during the past few decades (Wang et al., 2007). In this studied the Sn-3.5Ag-1.0Cu-0.1Zn solder was prepared via powder metallurgy route and aged at 150°C for 400 hours.

Sn–Pb solders for metal interconnections have a long history and continue to provide many benefits, such as ease of handling, low melting temperatures, good workability, ductility, and excellent wetting on Cu and its alloys (Suganuma, 2001). EU legislation, including Directive WEEE (Waste from Electrical and Electronic Equipment) and Directive RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment), prohibits the use of lead containing solders in many industries (Zivkovic et al., 2008). Researchers nowadays work on to remove the usage of lead with other potential candidate which also maintained the excellent properties of lead base product.

Lead-Free Solder

There are many types of lead-free solders available that have been used as a potential candidates as lead-based replacement in electronic industries such as Sn-Cu, Sn-Ag, Sn-Ag-Cu, Sn-Ag-Cu-Bi, Sn-Zn and Sn-Bi (Chiang et al., 2011). The addition of other metals was applied in order to reinforce solder characteristics.

Addition of Zinc

Study on the effects of minor additions of zinc on Cu substrate has been done by many researchers. They reported that the addition of Zinc has retarded the growth of intermetallic compounds (Cu_6Sn_5 and Cu_3Sn) (Cho et al., 2007). The minor Zn addition was found to be effective in reducing the amount of undercooling required for tin solidification and thereby to suppress the formation of large Ag_3Sn plates and also caused the changes in the bulk microstructure as well as the interfacial reaction (Kang et al., 2006).

Powder Metallurgy

A powder is defined as a finely divided solid, smaller than 1mm in its maximum dimension while powder metallurgy is the study of processing of metal powders, including the fabrication, characterization and conversion of metal powders into useful engineering components (German, 1994). Production of powder metallurgy parts involve mixing of elemental or alloy powders with additives and lubricants, compacting the mixture in a suitable die and heating the resulting green compacts in a controlled atmosphere furnace so as to bond the particles metallurgically. Powder metallurgy offers compositional flexibility, minimized segregation and the ability to produce graded microstructures with varying physical and mechanical properties. It also offers advantages over ingot metallurgy in terms of quality, cost, precision, productivity as well as by its ability to conserve critical raw materials through a high level of material utilization (Angelo & Subramanian, 2009).

Methodology

Sample Preparation

The raw sample of Sn-3.5Ag-1.0Cu-xZn (x: 0, 0.1) powders in micron size were weighed and placed in a small container. The mixing process was done using roll mill with constant speed of 200 rpm with mixing time of 2 hours to achieve a uniform distribution. The samples then compressed using hydraulic press with pressure of 110 bars to form cylindrical shape with diameter of 12 mm. Finally, the samples were then sintered in a furnace with nitrogen gas to reduce oxidation with a rate of 20^oC/min until the temperature increase to 150^oC for about 2 hours.

X-Ray diffraction (XRD) Test

The sample was go through XRD analysis to identify the phase formed and their distribution.

Mechanical Test

The Mitutoyo HM114 hardness testing machine with load of 0.01 N, speed of 10 µm/s and dwell time of 15 s was used in hardness test. For each samples, the average of 10 measurements was taken as microhardness value. The correlation between hardness and tensile properties which are yield strength and ultimate tensile strength can be calculate using equation (1) and (2) below (Salleh et al., 2011).

$$\sigma_y = -14.7 + 2.568 \text{ Hv (MPa)}. \quad (1)$$

$$\sigma_{UTS} = 65.8 + 2.563 \text{ Hv (MPa)}. \quad (2)$$

Intermetallic Study

For intermetallic study, the solder discs were melted on copper substrate with the aid of $ZnCl_2$ flux at temperature of 250^oC for a minute on a hot plate. The aging process was done for 100, 200, 300 and 400 hours in an oven at temperature of 150^oC. The solders were crossed section and mounted in an epoxy resin. The mounted samples were polished on silicon carbide paper followed by diamond polish to smooth the surface. The interfaces of the samples were observed under scanning electron microscope (SEM) and the elemental composition formed was confirmed by energy dispersive x-ray (EDX).

Intermetallic Thickness

The intermetallic thickness was measured using ImageJ software. The average thickness of the intermetallic was calculated by dividing the area with known micrograph length.

Data analysis and result

X-Ray diffraction (XRD) Test

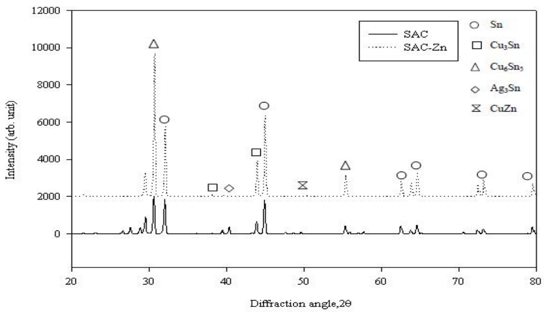

Figure 1: XRD profile for Sn-3.5Ag-1.0Cu solder

Mechanical Test

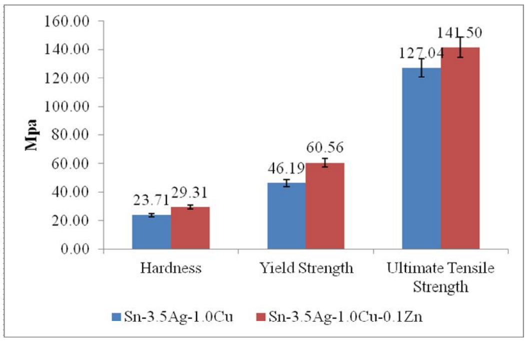

Figure 2: Mechanical properties of solder alloys

Intermetallic Study

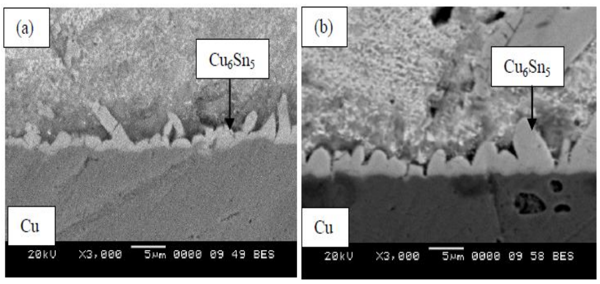

Figure 3: Phase Transformation for as-soldered (a) Sn-3.5Ag-1.0Cu and (b) Sn-3.5Ag-1.0Cu-0.1Zn

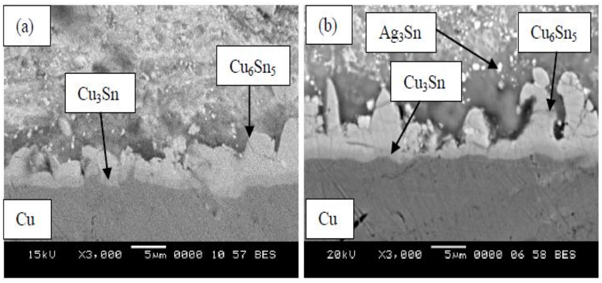

Figure 4: Phase Transformation for (a) Sn-3.5Ag-1.0Cu and (b) Sn-3.5Ag-1.0Cu-0.1Zn at 100 hours

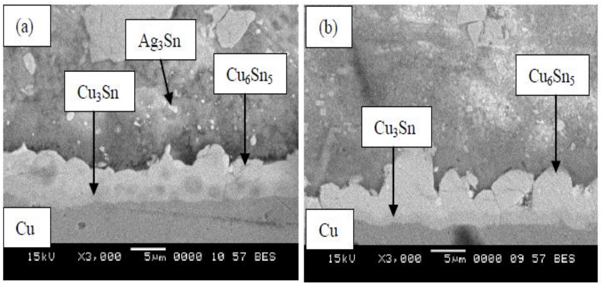

Figure 5: Phase Transformation for (a) Sn-3.5Ag-1.0Cu and (b) Sn-3.5Ag-1.0Cu-0.1Zn at 200 hours

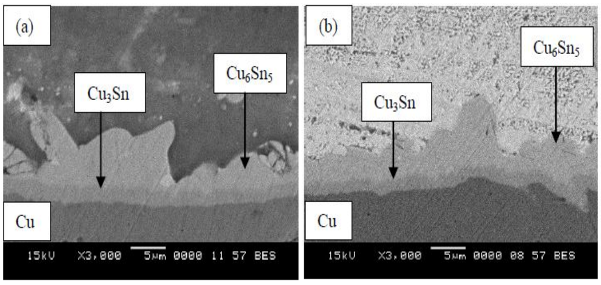

Figure 6: Phase Transformation for (a) Sn-3.5Ag-1.0Cu and (b) Sn-3.5Ag-1.0Cu-0.1Zn at 300 hours

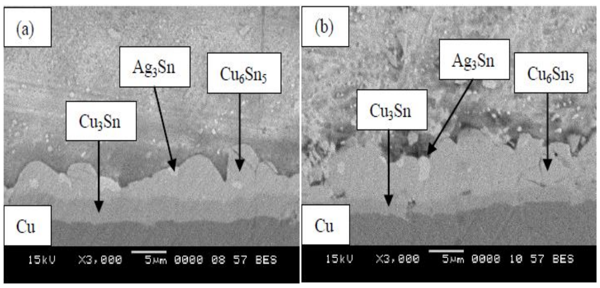

Figure 7: Phase Transformation for (a) Sn-3.5Ag-1.0Cu and (b) Sn-3.5Ag-1.0Cu-0.1Zn at 400 hours

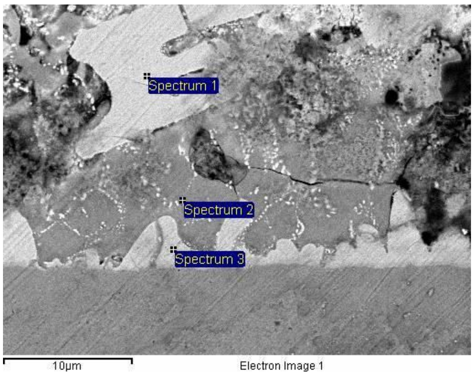

Figure 8: EDX analysis for as-soldered SAC

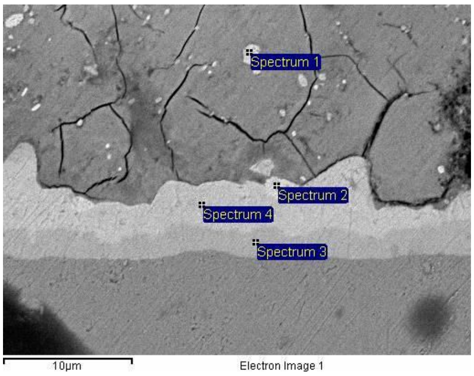

Figure 9: EDX analysis for SAC at 400 hours

Table 1: Elemental composition by EDX analysis for SAC

	Element, wt% (at%)			
	Sn	Ag	Cu	Phase
1	55.12 (39.67)	0.00 (0.00)	44.88 (60.33)	Cu_6Sn_5
2	78.76 (75.90)	19.10 (20.25)	2.14 (3.85)	β-Sn
3	58.83 (43.34)	0.00 (0.00)	41.17 (56.66)	Cu_6Sn_5

Table 2: Elemental composition by EDX analysis for SAC at 400 hours

	Element, wt% (at%)			
	Sn	Ag	Cu	Phase
1	64.40 (6085)	32.64 (33.64)	2.95 (5.21)	Ag_3Sn
2	100.00 (100.00)	0.00 (0.00)	0.00 (0.00)	β-Sn
3	60.69 (45.25)	0.00 (0.00)	39.31 (54.75)	Cu_3Sn
4	100.00 (100.00)	0.00 (0.00)	0.00 (0.00)	β-Sn

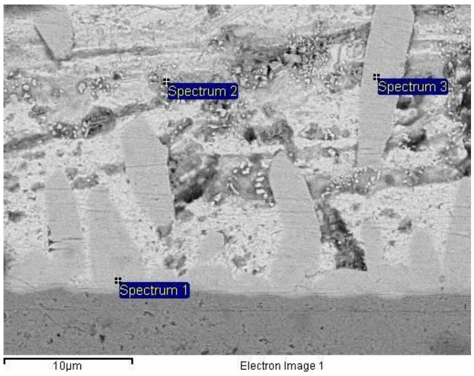

Figure 10: EDX analysis for as-soldered SAC-0.1Zn

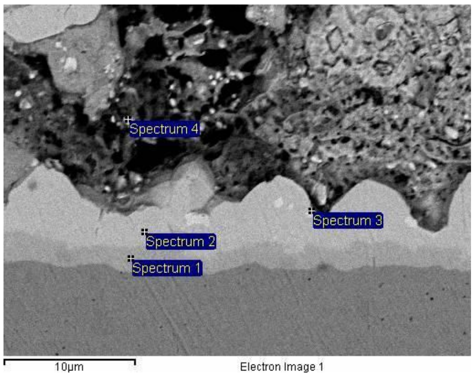

Figure 11: EDX analysis for SAC-0.1Zn at 400 hours

Table 3: Elemental composition by EDX analysis for as-soldered SAC-0.1 Zn

	Element, wt% (at%)				
	Sn	Ag	Cu	Zn	Phase
1	59.42 (43.98)	0.00 (0.00)	38.62 (53.39)	1.96 (2.63)	Cu_6Sn_5
2	88.87 (86.52)	6.42 (6.80)	3.72 (6.68)	0.00 (0.00)	Ag_3Sn
3	57.63 (42.16)	0.00 (0.00)	40.53 (55.40)	1.84 (2.44)	Cu_6Sn_5

Table 4: Elemental composition by EDX analysis for SAC- 0.1Zn at 400 hours

	Element, wt% (at%)				
	Sn	Ag	Cu	Zn	Phase
1	34.08 (21.70)	0.00 (0.00)	62.77 (74.65)	3.15 (3.65)	Cu_3Sn
2	53.93 (38.57)	0.00 (0.00)	42.99 (57.43)	3.08 (4.00)	Cu_6Sn_5
3	47.81 (35.40)	13.28 (10.82)	37.72 (52.18)	1.18 (1.59)	Cu_6Sn_5
4	87.99 (81.37)	2.97 (3.03)	9.04 (15.61)	0.00 (0.00)	β-Sn

Intermetallic Thickness

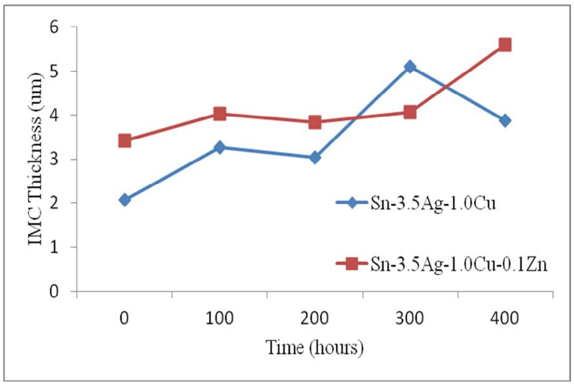

Figure 12: Cu_6Sn_5 Intermetallic thickness

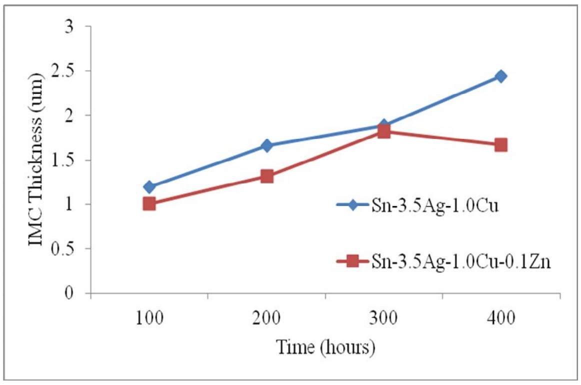

Figure 13: Cu_3Sn Intermetallic thickness

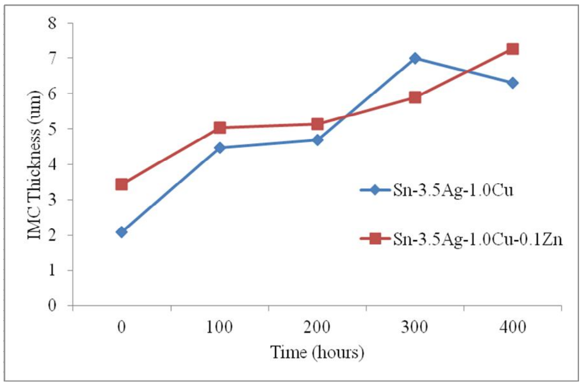

Figure 14: Total Intermetallic (IMC) thickness of Sn-3.5Ag-1.0Cu and Sn-3.5Ag-1.0Cu-0.1Zn

Discussions

X-Ray diffraction (XRD) Test

Figure 1 present the phase distribution pattern under XRD analysis for Sn-3.5Ag-1.0Cu and Sn-3.5Ag-1.0Cu-0.1Zn after sintering process. The main phase produced were Cu_6Sn_5, Cu_3Sn and β-Sn because Sn is the major constituent and it reacted with Cu substrate to form such phase compound. There were CuZn and Ag_3Sn phase in the solder as well. These phases seem formed during solder preparation.

Mechanical Test

Figure 2 shows the mechanical properties of Sn-3.5Ag-1.0Cu (SAC) and Sn-3.5Ag-1.0Cu-0.1Zn (SAC-Zn) solder alloys. The hardness, yield strength and ultimate tensile strength for SAC-Zn is high compared to SAC alloy. According to Kamal and Gouda, this increase can be attributing to the formation of the hard Ag_3Sn and AgZn compounds, which act as hard inclusions in the soft matrix (Kamal & Gouda, 2008). The Zn has enhanced the mechanical strength thus provide better properties of solder alloy.

Intermetallic Study

Figure 3 to 7 shows the formation of intermetallic on Cu substrate. For SAC and SAC-Zn as-soldered samples showed in Figure 3 (a) and (b), only a single IMC formed which is Cu_6Sn_5.This phase formation has been confirm by EDX analysis in Figure 8 for SAC and Figure 10 for SAC-0.1Zn, while their elemental distribution was shown in Table 1 and 3 respectively. The Cu_6Sn_5 IMC formed was in scallop shape and it has been suggested that a ripening process contributes to the formation of the scallop structure of the Cu_6Sn_5 (Kim et al., 1995). Wang reported that the surface morphology of the Cu-Zn appears to have a granular appearance on the surface of Sn-Ag-Cu-Zn/Cu, but the grain size of Cu_5Zn_8 is far smaller compared to Cu_6Sn_5 thus may not observable by SEM image (Wang, et al., 2007).

As the aging process reach 100 hours, formation of another phase which is Cu_3Sn near the Cu substrate can be seen as shown in Figure 4(a) and (b). The Cu_6Sn_5 was thicker compared to Cu_3Sn as shown by plotted graph in Figure 14 .When the aging time increases to 200 and 300 hours, more rapid and quite distinctive darker layer of Cu_3Sn IMC can be seen as shown in Figure 5 and 6 with planar morphology while the morphology of Cu_6Sn_5 slowly change to planar structure as well.

The morphology of Cu_6Sn_5 gradually transform from the scallop-type to planar type when aging time increase to 400 hours (Figure 7). This transformation may be due to change in interfacial energy. The scallop morphology has a larger interfacial area than the planar interface. So the intermetallic compounds transform to reduce the interfacial energy (Mayappan, 2012; Mayappan et al., 2009). At this aging time, the Cu_6Sn_5 IMC and total IMC started to suppress by Zinc addition. Beside Cu_6Sn_5 and Cu_3Sn, there was another phase formed in the solder system and proved as Ag_3Sn by EDX analysis shown in Figure 8 and 9 for SAC and in Figure 10 and 11 for SAC-Zn together with their elemental distribution in Table 1 to 4 respectively.

Intermetallic Thickness

The intermetallic thickness was measured by Image J software and the graph was plotted. Figure 12 and 13 shows the intermetallic thickness of Cu_6Sn_5 and Cu_3Sn respectively for SAC and SAC-Zn solder under aging progress. Figure 14 shows total IMCs thickness ($Cu_6Sn_5 + Cu_3Sn$) for both solders system.

Generally the intermetallic layer grows thicker as aging time increase. For as-soldered solder SAC and SAC-0.1Zn, the Cu_6Sn_5 IMC formed with thickness of 2.08µm and 3.4µm respectively. The total intermetallic thickness at 100 hours aging ware 4.46µm and 5.03µm for both solder system respectively. The total IMC thickness for both solder system keep increased when aging time reach 200 hours with thickness of 4.7 µm for SAC and 5.15µm for SAC-0.1Zn while at 300 hours their total thickness were 6.99µm and 5.89µm respectively. Unfortunately, at 400 hours, there was slightly decreasing trend for SAC intermetallic thickness which was 6.31µm, but the thickness for SAC-0.1Zn increase to 7.25µm.

The evolution of Cu-Sn IMCs for Sn-Ag-Cu/Cu couples is based on continuous growth of Cu_6Sn_5 and Cu_3Sn (Wang, et al., 2007). According to Kang, minor addition of Zn to SAC was very effective for reducing the IMC growth on Cu pads (Kang, et al., 2006). However, in this study Zn addition has reduced the Cu_3Sn intermetallic thickness but inadequate to suppress the Cu_6Sn_5 IMC and total intermetallic thickness.

Conclusions

The addition of 0.1 wt% Zn into the Sn-3.5Ag-1.0Cu has been studied. The mechanical properties of the SAC-Zn solder have been improved compared to the Sn-Ag-Cu solder. Two type of intermetallic were formed which are Cu_6Sn_5 and Cu_3Sn, while Ag_3Sn phase compound was accumulate in the solder system. The intermetallic phase for Cu_3Sn was in planar structure while the Cu_6Sn_5 phase transform from scallop-type to planar-type as aging time increase. The addition of Zn has reduced the Cu_3Sn intermetallic thickness although the total intermetallic thickness is higher compared to the undoped solder.

Acknowledgment

The work describe in this paper was fully supported by a grant from Dana Kecemerlangan, [600-RMI/ST/DANA 5/3/Dst (456/2011)]

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