

## Growth of Cu-Zn<sub>5</sub> and Cu<sub>5</sub>Zn<sub>8</sub> Intermetallic Compounds in the Sn-9Zn/Cu Joint During Liquid State Aging

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**Abstract**— The phase and intermetallic thickness of Cu-Zn<sub>5</sub> and Cu<sub>5</sub>Zn<sub>8</sub> has been investigated under liquid state aging using reflow method. Both the intermetallic was formed by reacting Sn-9Zn lead free solder with copper substrate. Scanning electron microscope (SEM) was used to see the morphology of the phases and energy dispersive x-ray (EDX) was used to estimate the elemental compositions of the phases. The morphology of the Cu<sub>5</sub>Zn<sub>8</sub> phase was rather flat but when the soldering temperature and time increases, the morphology becomes scallop. Intermetallic thickness measurements show that the thickness of the Cu-Zn<sub>5</sub> decreases with increasing soldering time and temperature. Whereas, the thickness of the Cu<sub>5</sub>Zn<sub>8</sub> intermetallic increases with soldering time and temperature.

**Keywords**— Cu<sub>5</sub>Zn<sub>8</sub> Intermetallic, Lead-free Solder, Sn-Zn Solder.

### I. INTRODUCTION

Lead-based solders are widely used in the electronic industries because of their unique material properties and low-cost [1]. Unfortunately lead and its compound are toxic to the human body and cause serious environmental problems. Thus, the development of lead-free solders is in progress.

Among the Sn-based solder alloys, the Sn-Zn solder has been considered as a suitable candidate because of its low melting temperature of 198°C [2]. Many studies have been published on this solder as a binary solder or by adding third element into it [3, 4].

During soldering, the solder material will react with the Cu substrate and forming interface termed intermetallic

compound (IMC). For Sn-Zn solders reacting with Cu, it is estimated that the first forming phase is  $\gamma$ -Cu<sub>5</sub>Zn<sub>8</sub> when soldering was done at 250°C [5].

Although, the formation of these interface intermetallics is desirable to help attain good bonding between the substrate and the solder, but there are some drawbacks. The intermetallics are quite brittle and excessive thickness may degrade the interfacial strength and the mismatch in physical properties such as thermal expansion coefficient and the elastic modulus [6].

This study investigates the microstructural evolution and the thickness of Cu<sub>5</sub>Zn<sub>8</sub> and Cu-Zn<sub>5</sub> intermetallics layer in the Sn-9Zn/Cu Cu couple under liquid state aging using reflow method.

### II. METHODOLOGY

Solder/copper joint were made by reflowing 0.2 g solder on Cu substrate. The solder/Cu with some ZnCl<sub>2</sub> flux were placed on the hot plate and subsequently heated to a maximum temperature of 290, 310 and 320°C. The soldering time were set at 1, 3, 5, 10 and 15 minutes.

After soldering, the specimens were left on the hotplate to cool and removed upon reaching 50°C. The samples were then cleaned using soap. The samples were cross sectioned using low speed diamond cutter and mounted using epoxy resin. The mounted samples were mirror polished and etched. The Cu/solder/Cu interface was then analyzed under Scanning Electron Microscope (SEM) operating in backscatter mode. For each sample, 2-3 micrographs were taken. To identify the elemental compositions of the phases, EDX was used in backscatter mode. To determine the average thickness of the intermetallic layers, the total area of the layer was calculated using ImageJ software and then divided by the known micrograph length with an accuracy of  $\pm 0.01 \mu\text{m}$ .

### III. RESULTS AND DISCUSSIONS

#### A. Intermetallic Formation

The interface between the Sn-9Zn solder alloy and Cu substrate showed Zn-rich phase with tiny holes all along the solder joint. The Sn-9Zn alloy has a eutectic composition. The solubility of Zn in Sn is very low. The Zn-rich phase was not able to form a solid solution with Sn and precipitate as a needle-like second phase in the solder alloy. Micro voids were formed at the interface between the solder alloy and Cu substrate [11].

Shown in Figures 1 to 3 are the intermetallic formation after soldering for 1 minutes at 290, 310 and 320°C, respectively. In Figures 1 and 2, only (Cu-Zn<sub>5</sub>)[8,9] intermetallic was formed and in Figure 3, both (Cu-Zn<sub>5</sub>) and Cu<sub>5</sub>Zn<sub>8</sub> was observed.

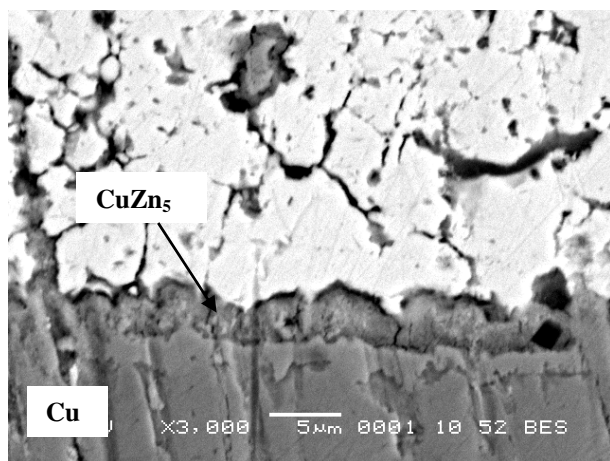


Figure 1: IMC layer between solder/Cu joints after soldering for 1 minute at 290°C.

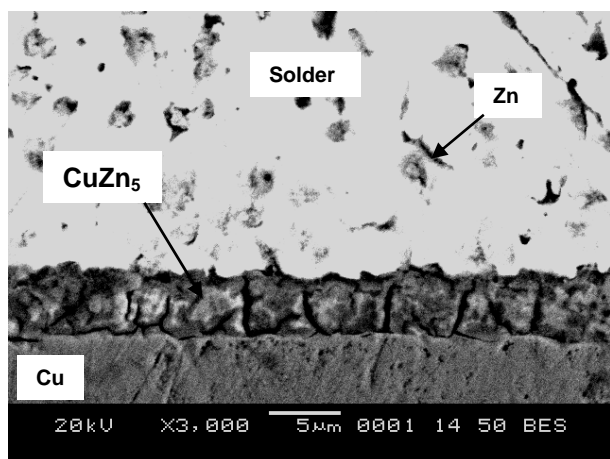


Figure 2: IMC layer between solder/Cu joints after soldering for 1 minute at 310°C.

The reaction product during wetting, i.e., the first compound forming at the interface should have the highest driving force for formation [10]. Lee et al. [10] predicted

using thermodynamic calculations that the driving force for Cu<sub>5</sub>Zn<sub>8</sub> phase is larger than that of (Cu-Zn). A liquid state aging conducted by Lee and Shieu [11] on Sn-9Zn/Cu system found out that the activation energy for the formation of (Cu-Zn) and Cu<sub>5</sub>Zn<sub>8</sub> are 31 and 26 kJ/mol, respectively, for 230-270°C temperature range. Accordingly, it can be predicted that the first-forming compound at the interface between Sn-Zn solder and Cu substrate is Cu<sub>5</sub>Zn<sub>8</sub> phase with still a strong possibility for (Cu-Zn) phase to precipitate further at the interface.

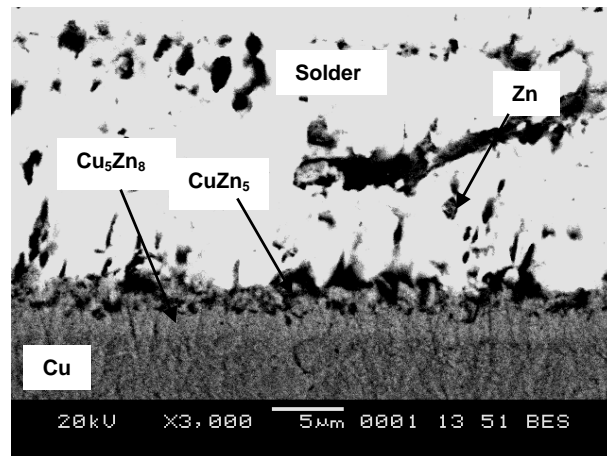


Figure 3: IMC layer between solder/Cu joints after soldering for 1 minute at 320°C.

When the soldering time increases, the growth of the Cu-Zn<sub>5</sub> intermetallic is insignificant while the Cu<sub>5</sub>Zn<sub>8</sub> intermetallic grew thicker in a flat morphology as shown in Figures 4-6.

From EDX analysis, Sn atoms are not found within the γ-Cu<sub>5</sub>Zn<sub>8</sub> intermetallic. So, the Cu<sub>5</sub>Zn<sub>8</sub> intermetallic may act as a diffusion barrier for Sn atoms from diffusing from the solder to the Cu substrate to form Cu<sub>6</sub>Sn<sub>5</sub>.

It is known that the diffusion constant of Cu atoms in Sn is higher than that of Zn atoms in Sn matrix [10]. The growth mechanism of Cu<sub>5</sub>Zn<sub>8</sub> phase is due to the very fast diffusion of Cu atoms into the solder matrix. Considering Cu atoms are supplied adequately in the intermetallic layer due to their rapid diffusion, the diffusion of Zn atoms toward the joint interface controls the growth of the Cu-Zn compound.

Figure 5 (c & d) shows the formation some cracks within the Cu<sub>5</sub>Zn<sub>8</sub> intermetallic and some Sn diffused past the Cu<sub>5</sub>Zn<sub>8</sub> intermetallic and moved towards the Cu substrate. The diffusion of the Sn is very obvious when soldering was done at 320°C, as shown in Figure 6(a). EDX analysis on this spot (Figure 5(c)) is shown in Figure 7 and the elemental composition on the spot is listed in Table 1. It shows the present of Cu with some Sn and very little Zn.

There is a possibility that the present of Sn and Cu will lead to the formation of  $\text{Cu}_6\text{Sn}_5$  intermetallic at the later stage of aging as reported by some researchers [3,4]

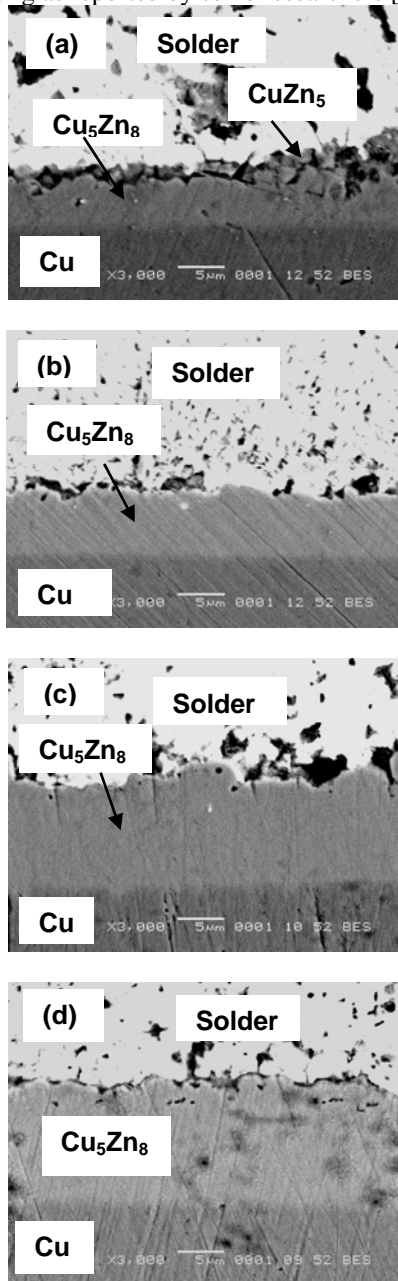


Figure 4: Intermetallic formation soldering at 290°C for (a) 3, (b) 5, (c) 10 and (d) 15 minutes

### B. Intermetallic Thickness

When soldering was done at 290°C, the Cu-Zn<sub>5</sub> intermetallic has thickness around 2 μm. This intermetallic thickness decreases as the soldering temperatures increases as shown in Figure 8. At higher soldering temperature the Cu rich phase, Cu<sub>5</sub>Zn<sub>8</sub> starts to form and this reduces the Cu-Zn<sub>5</sub> phase which formed away from the Cu substrate.

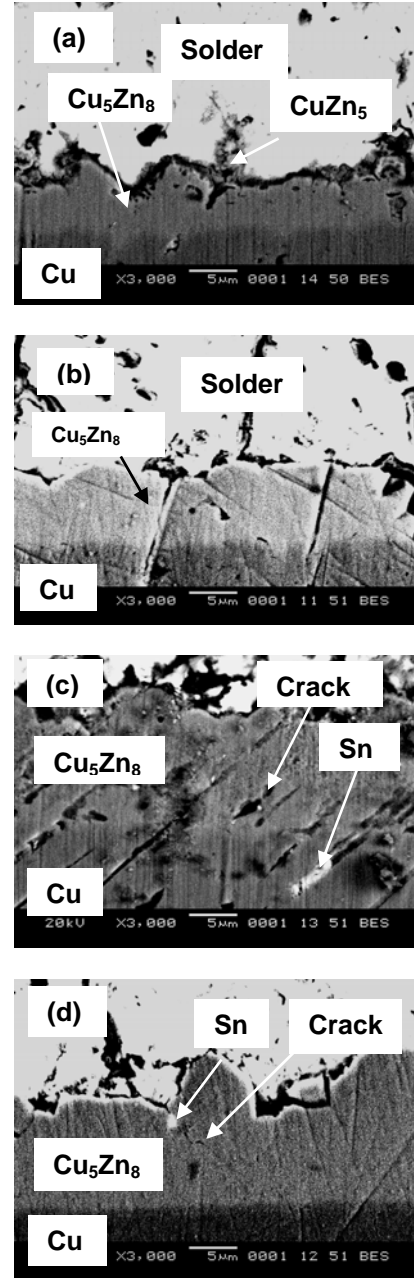


Figure 5: Intermetallic formation soldering at 310°C for (a) 3, (b) 5, (c) 10 and (d) 15 minutes

With increasing soldering temperature and time, the thickness of the Cu<sub>5</sub>Zn<sub>8</sub> intermetallic grows progressively as shown in Figure 9. When soldering was done at 1, 3, 5 and 10 minutes, the different soldering temperature do not effect the intermetallic thickness. The values are within the experimental error. Only during soldering at 320°C, for 15 minutes there is a big different in the thickness.

soldering was done at 310 and 320°C. On the other hand, the thickness of the  $\text{Cu}_5\text{Zn}_8$  phase grew progressively as the soldering temperature and time increases.

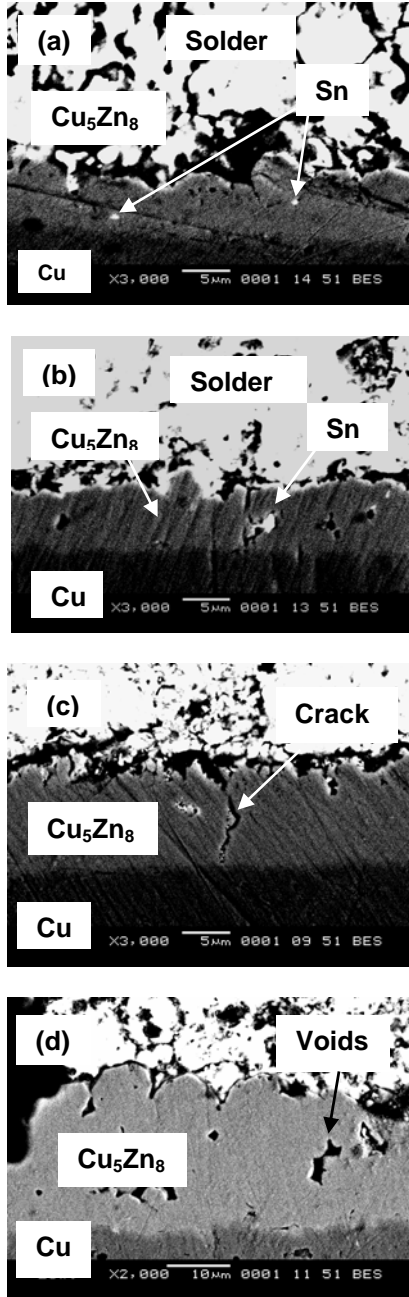


Figure 6: Intermetallic formation soldering at 320°C for (a) 3, (b) 5, (c) 10 and (d) 15 minutes

#### IV. CONCLUSION

The phase formation and thickness of the intermetallic compound layer at the Cu-solder interface in Sn-9Zn/Cu system solder joints during liquid state aging were investigated. The intermetallic layers consisted of Cu-Zn<sub>5</sub> and  $\text{Cu}_5\text{Zn}_8$  phases at lower soldering temperature and time. The Cu-Zn<sub>5</sub> phase disappears as the aging progresses. At higher soldering and time, the Sn starts diffuse towards the Cu substrate and the cracking of the  $\text{Cu}_5\text{Zn}_8$  starts to happen. The thickness of the Cu-Zn<sub>5</sub> phase was around 2µm and during soldering at 290°C and decrease when

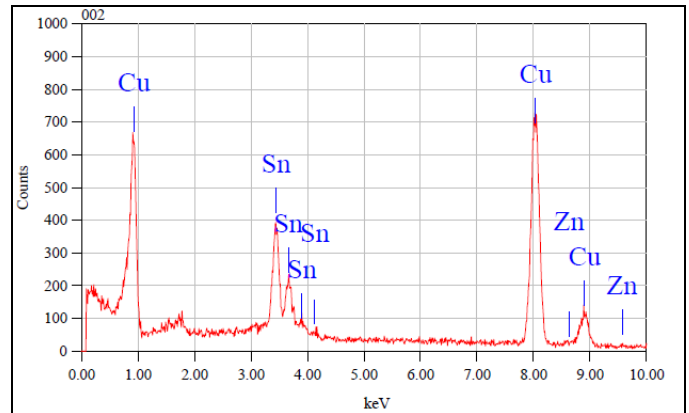


Figure 7: EDX analysis on a spot labeled “Sn” in figure 5(c)

Table 1: Elemental composition of a spot labeled “Sn” in figure 5(c)

	Mass%	atomic%
Cu	82.82	89.69
Zn	0.75	0.79
Sn	16.43	6.52

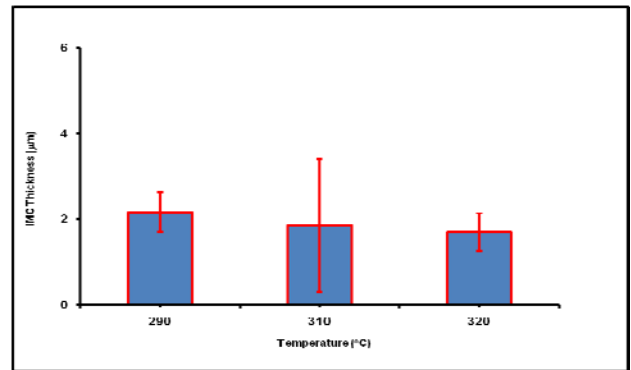


Figure 8:  $\text{CuZn}_5$  intermetallic soldering for 1 minute

#### ACKNOWLEDGEMENT

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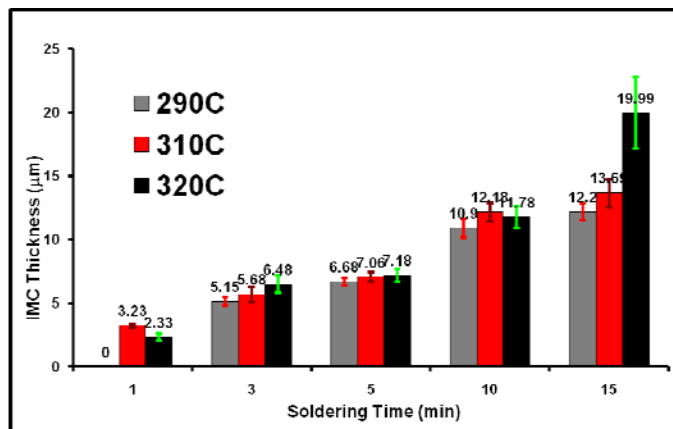


Figure 9: intermetallic thickness at different soldering time temperatures

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