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The Microstructure Evolution and Activation Energy Study of Cu_6Sn_5 and Cu_3Sn Intermetallic Compound Layer of Sn-10Cu/Cu Solder Joint

Muhammad Amirul Aiman A. Ramlee[a], Rita Mohd Said[a*], Nur Syahirah Mohamad Zaimi[a] and Norainiza Saud[a]

[a]*Faculty of Chemical Engineering & Technology, University Malaysia Perlis, 02600 Jejawi Perlis*
∗Corresponding author. Tel.: +604-9798751; fax: +604-9798755; e-mail: rita@unimap.edu.my

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ABSTRACT

The electronic packaging industry is gradually moving away from lead solder to lead-free solder, which is more environmentally friendly. However, there is still work to be done to ensure that lead-free solder meets the demands and requirements of the latest technology. The present study demonstrates the analysis of the microstructure formation of Cu_6Sn5 and Cu_3Sn intermetallic compound layers in Sn-10Cu/Cu solder joints. Therefore, the key objective of this research is to determine the growth rate and activation energy of the Cu_6Sn_5 and Cu_3Sn intermetallic compound layer of the Sn-10Cu/Cu solder joint. The investigation on the bulk solder microstructure which consists of Cu_6Sn_5 and Cu_3Sn intermetallic compound layer was carried out using Optical Microscope (OM), Scanning Electron Microscope (SEM) with EDX and ImageJ software. The IMC layer undergoes rapid growth with increasing aging temperature and duration and the two main IMC layers (Cu_6Sn_5 and Cu_3Sn) grew thicker. The growth kinetic solder joints for Sn-10Cu and Sn-0.7Cu are 22.44 kJ/mol and 31.20 kJ/mol, respectively. Hence, the findings from this study may offer useful information for the development of high-reliability solder joints in future applications.

Keywords: *Sn-10Cu, Sn-0.7Cu solder paste, Bulk Microstructure, Intermetallic Compound, Activation energy*

1. INTRODUCTION

Soldering is a metallurgical joining method that employs filler metal, which is the solder itself, which melts at temperatures below 425°C. Fundamentally, solder serves as connection materials in ensuring electrical, mechanical and thermal continuity of the connections between the devices and substrates [1]. Previously, tin-lead (Sn-Pb) solders are widely used as the main solder interconnections in the electronic industry [2], [3]. This was owing to their low melting point of 183 °C, good electrical conductivity, excellent wettability and low cost of Sn-Pb solder alloy [2], [4]. However, the lead (Pb) content in solder is very toxic and harmful to human health and the environment. Due to these issues, the employment of Pb in the electrical devices has been banned through the Restriction of Hazardous Substance (RoHS) directive enacted by the European Union, starting July 1, 2006 [5]. Therefore, great efforts have been made by academicians as well as industries to replace Pb solder alloys with to lead-free solder alloys.

Near eutectic Sn-0.7Cu solder alloys have become interesting and widely used in the electronics industry, owing to their low melting point, reasonable cost, good fluidity and wettability [6]. Meanwhile, Sn-Cu solder alloys with high Cu content have become a potential candidate in high-temperature solder applications [7]. According to the equilibrium phase diagram of Sn-Cu, a peritectic reaction will occur during the cooling process of Sn-10Cu solder alloys [7], [8]. Fundamentally, the typical phases that will be formed with this composition are the intermetallic compounds (IMCs) of ε (Cu_3Sn) and η (Cu_6Sn_5). It has been reported that, the Cu_3Sn phase is more brittle and susceptible to failure as compared to Cu_6Sn_5 [8]. Therefore, it is beneficial to elucidate the growth kinetics of Cu_3Sn and Cu_6Sn_5 in existing Sn-0.7Cu and Sn-10Cu solder joints subjected to reflow soldering and isothermal aging. In this paper, the microstructure evolution and activation energy between Cu_3Sn and Cu_6Sn_5 IMCs in Sn-0.7Cu/Cu and Sn-10Cu/Cu will be evaluated under reflowed and isothermal aging conditions.

2. MATERIALS AND METHODS

In this research, solder powder of Sn-0.7 wt.% Cu with an average particle size of ~ 45 µm (supplied by Nihon Superior Co. Ltd, Japan) was used as the base material matrix. The solder powder was mixed with flux, resulting in Sn-0.7 wt.% Cu solder paste. Then, Sn-0.7 wt.% Cu solder paste was mixed with 9.3 wt.% copper powder to obtain Sn-10 wt.% Cu solder paste. To ensure the homogeneity between the Sn-0.7 wt.% Cu and copper powder added, the mixing process was carried out for about 30 minutes. Consequently, the solder paste was attached to the Cu substrates and underwent a reflow soldering process in a desktop reflow oven. Then, the reflowed samples were isothermally aged at different temperatures and times which are 75 °C, 125 °C, and 150 °C for 24, 72, and 168 hours respectively. Then, all the samples were mounted and cross-sectioned for the ex-situ microstructure analysis. The microstructure analysis of Sn-10 wt.% Cu and Sn-0.7 wt.% Cu solder paste was studied using an Optical Microscope

(OM). The analysis included observation of the microstructure of bulk solder and intermetallic compound (IMC) layer formation. The interfacial IMC layer thickness was measured by using Equation (1):

$$t = A/L \quad (1)$$

where the thickness (t) was obtained by dividing the IMC area (A) with the total IMC length (L) that had existed along the interface. Five micrographs were taken from each of the samples to determine the average thickness of tthe IMC layer.

3. RESULTS AND DISCUSSIONS

Figure 1 to Figure 3 show the microstructure at the bulk solder of Sn-0.7 wt.% Cu/Cu solder joint exposed to different isothermal aging temperatures for 0, 24, 72, and 168 hours respectively. According to the finding obtained, the microstructure of Sn-0.7 wt.% Cu/Cu solder joint consists of β-Sn and Cu_6Sn_5 / β-Sn areas. In the as-reflowed solder joint, the Cu_6Sn_5 phase undergoes coarsening under different temperatures of isothermal aging. Meanwhile, at 150 °C the β-Sn phase undergoes reduction. With an increase in the aging temperature, the Cu_3Sn phase disintegrates which allows the Cu_6Sn_5 phase to rapidly grow. This refers to the process by which the Cu_3Sn phase breaks down or decomposes into other phases or components. It means that, at higher aging temperatures, the Cu_3Sn phase loses its structural integrity and transforms into other phases or materials.

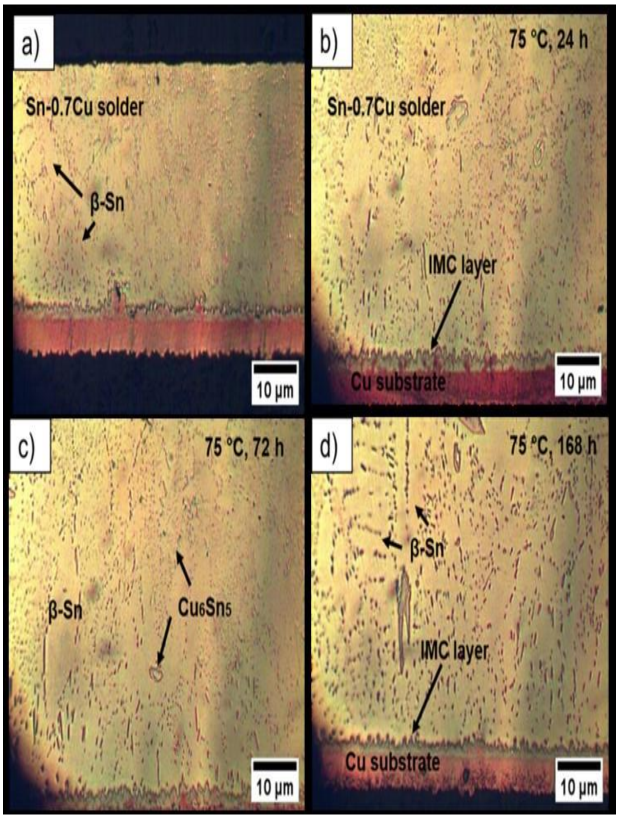

Figure 1. Bulk solder microstructure of Sn-0.7 wt.% Cu/Cu subjected to isothermal aging at 75°C (a) 0h (b) 24h (c) 72h (d) 168h.

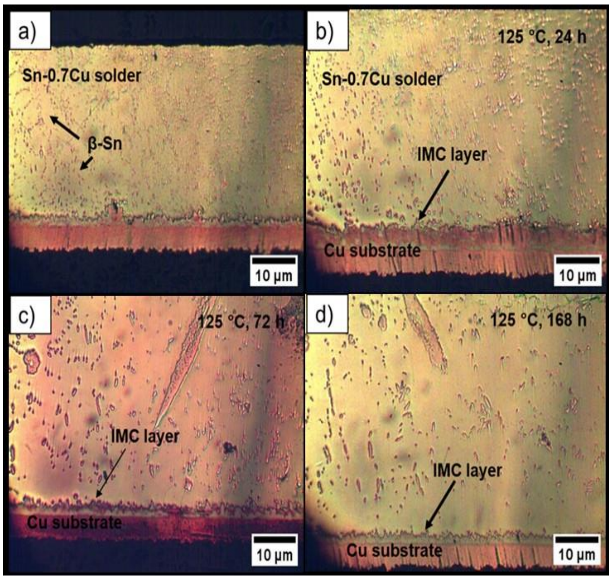

Figure 2. Bulk solder microstructure of Sn-0.7 wt.% Cu/Cu subjected to isothermal aging at 125°C (a) 0h (b) 24h (c) 72h (d) 168h.

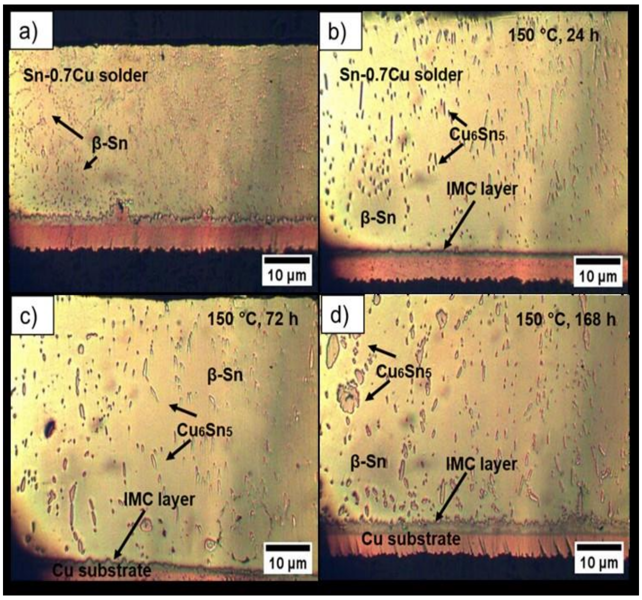

Figure 3. Bulk solder microstructure of Sn-0.7 wt.% Cu/Cu subjected to isothermal aging at 150°C (a) 0h (b) 24h (c) 72h (d) 168h.

Figure 4 to Figure 6 show the microstructure at the bulk solder of Sn-10 wt.% Cu/Cu solder joints subjected to different isothermal aging temperaturesfor 0, 24, 72, and 168 hours respectively. Based on the figures, the microstructure of the Sn-10 wt. %Cu/Cu solder joint consists of β-Sn and Cu_3Sn / β-Sn areas. However, as the samples were subjected to different temperatures of isothermal aging, the coarsening of the Cu_3Sn phase at the bulk microstructure was observed. Based on the observation, at 150 °C the β-Sn phase area was reduced. With the increase in aging temperature, the Cu_6Sn_5 phase disintegrates which allows the Cu_3Sn phase to rapidly grow. The Ostwald ripening theory also states that the driving force for grain growth is heavily dependent on the grain boundary which possesses high potential energy [9].

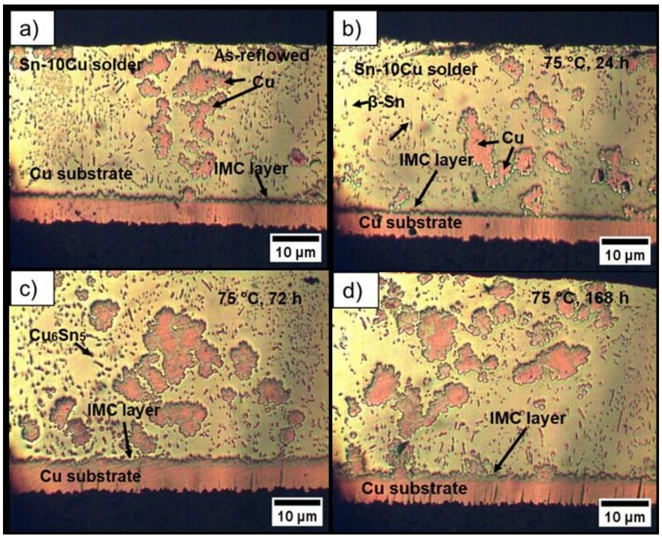

Figure 4. Bulk solder microstructure of Sn-10 wt.% Cu/Cu subjected to isothermal aging at 75°C (a) 0h (b) 24h (c) 72h (d) 168h.

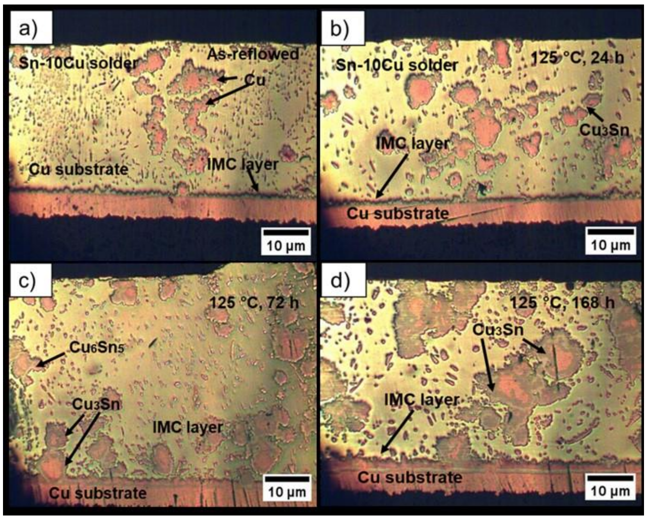

Figure 5. Bulk solder microstructure of Sn-10 wt.% Cu/Cu subjected to isothermal aging at 125°C (a) 0h (b) 24h (c) 72h (d) 168h.

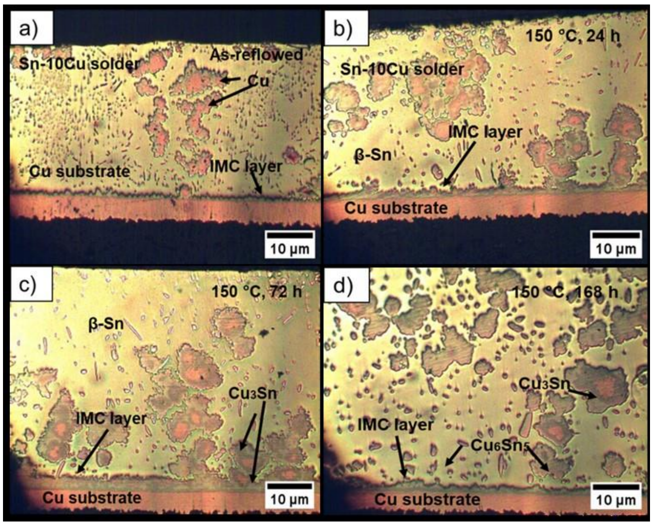

Figure 6. Bulk solder microstructure of Sn-10 wt.% Cu/Cu subjected to isothermal aging at 150°C (a) 0h (b) 24h (c) 72h (d) 168h.

Figure 7 to Figure 12 depict the formation of the interfacial IMC layer for both Sn-0.7 wt.% Cu/Cu and Sn-10 wt.% Cu/Cu solder joints subjected to isothermal aging. Based on the observation, the morphology of the IMC layer consists of a discontinuous scallop shape. According to Lee et al., two interfacial zones known as Cu_6Sn_5 and Cu_3Sn form at the intermetallic layer of the solder joint [10]. Previous researchers found that the Cu_6Sn_5 phase is the first phase and exhibits a scalloped pattern. The Cu_3Sn, on the other hand, is more layered and develops at the intermetallic layer contact. While the Cu_3Sn phase is substantially smaller, the thickness of both phases varies. IMCs in this study develop in response to temperature and the passage of time. This could be due to a diffusion-controlled process where Cu and Sn atoms migrate to form the Cu_3Sn compound at these interfaces. Cu_3Sn could be a compound with a specific crystal structure that naturally leads to a layered or lamellar structure. This layered structure can be explained by the arrangement of Sn and Cu atoms in a specific crystal lattice or by the formation of specific crystallographic planes that lead to layering. Besides, several factors hinder phase sizing change such as thermodynamics factor, kinetic factors and competition for reactants [11].

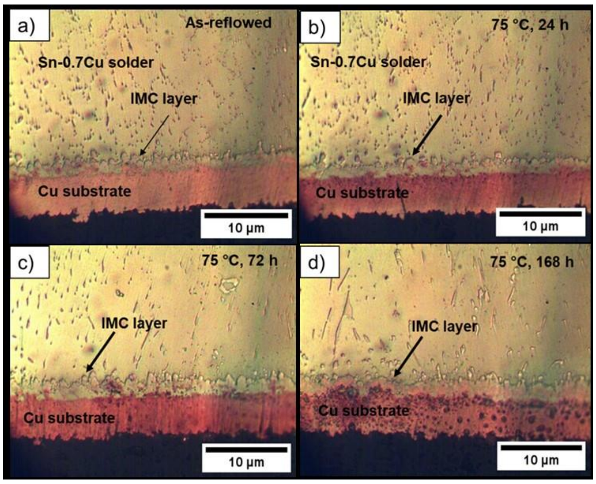

Figure 7. Interfacial IMC of Sn-0.7Cu wt.% Cu/Cu subjected to isothermal aging at 75°C (a) 0h (b) 24h (c) 72h (d) 168h.

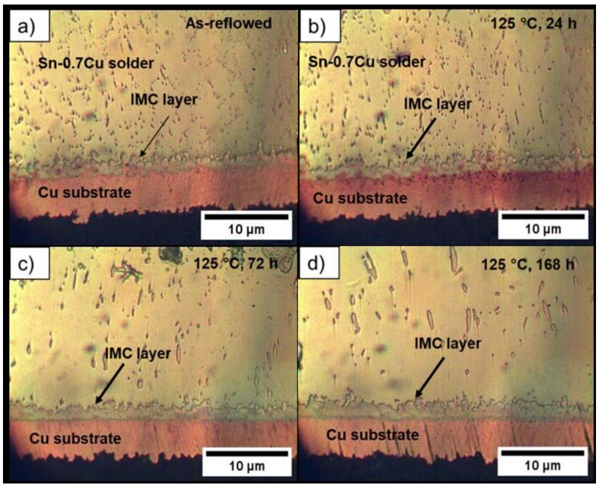

Figure 8. Interfacial IMC of Sn-0.7Cu wt.% Cu/Cu subjected to isothermal aging at 125°C (a) 0h (b) 24h (c) 72h (d) 168h.

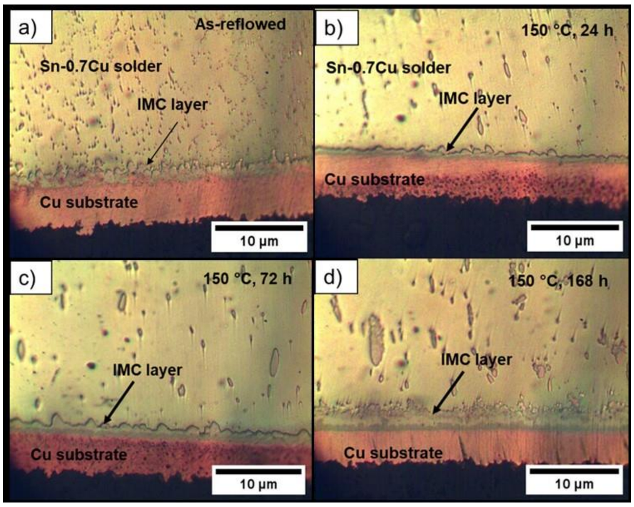

Figure 9. Interfacial IMC of Sn-0.7Cu wt.% Cu/Cu subjected to isothermal aging at 150°C (a) 0h (b) 24h (c) 72h (d) 168h.

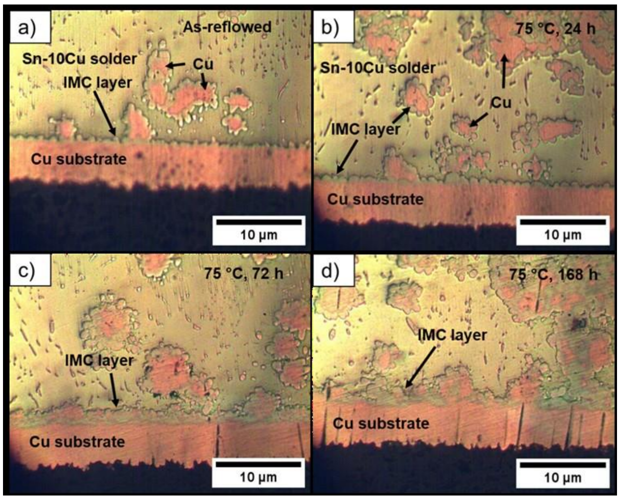

Figure 10. Interfacial IMC of Sn-10 Cu wt.% Cu/Cu subjected to isothermal aging at 75°C (a) 0h (b) 24h (c) 72h (d) 168h.

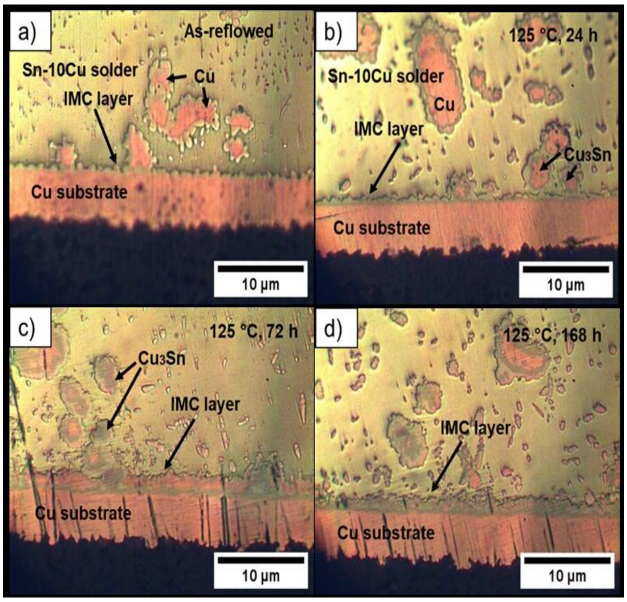

Figure 11. Interfacial IMC of Sn-10 Cu wt.% Cu/Cu subjected to isothermal aging at 125°C (a) 0h (b) 24h (c) 72h (d) 168h.

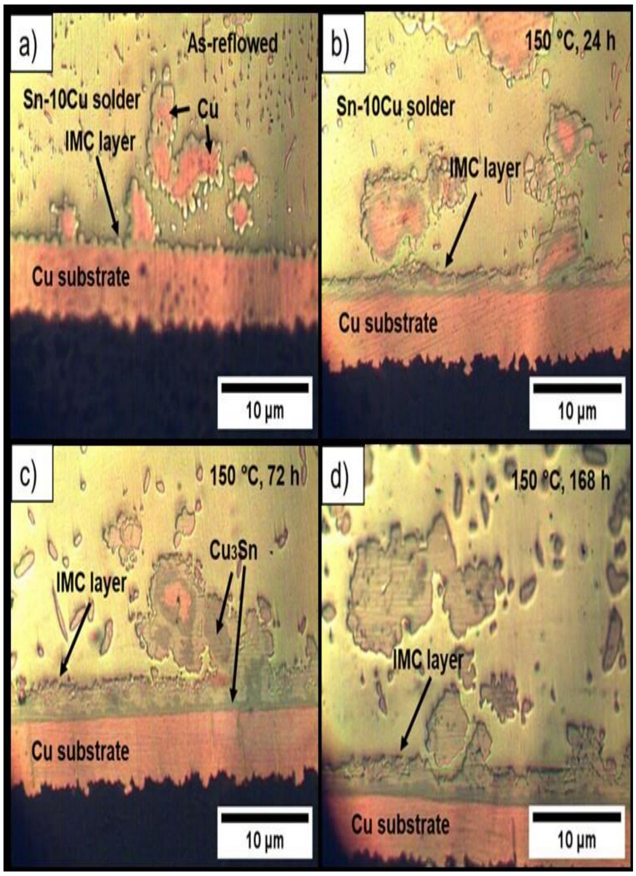

Figure 12. Interfacial IMC of Sn-10 Cu wt.% Cu/Cu subjected to isothermal aging at 150°C (a) 0h (b) 24h (c) 72h (d) 168h.

The evolution of the interfacial IMC morphology at 75°C, 125°C, and 150°C. Clearly, Cu_6Sn_5 and Cu_3Sn layers could be seen at the solder/Cu interface under a specific situation. It was discovered that when the Cu_6Sn_5 layer aged, it changed from being scallop-like to becoming planar-like. This may be because the distance between the scallop peaks and the Cu substrate is greater than the distance between the scallop valleys and the Cu substrate. As a result, Cu atoms will diffuse to the scallop valley more quickly than they will to the scallop peak, causing the valley to expand more quickly and the Cu_6Sn_5 layer to eventually become planar [12].

Figure 4.13 to Figure 4.16 depict the relationship between the thickness of the IMC layer and the square root of the aging time for Sn-10 wt.% Cu and Sn-0.7 wt.% Cu solder joints. The graph illustrates a linear correlation between the aging time and the thickness of the IMC layer. According to the previous finding, the correlation between the thickness of the IMC layer and aging time generally follow Fick's law [10];

$$y = \sqrt{Dt} \quad (2)$$

where y is the average IMC thickness of the layer, t is the aging time, and D is the growth rate. The growth rate could be determined from a linear regression analysis of y versus $\sqrt{t}$, where the slope of the straight line is $\sqrt{D}$.

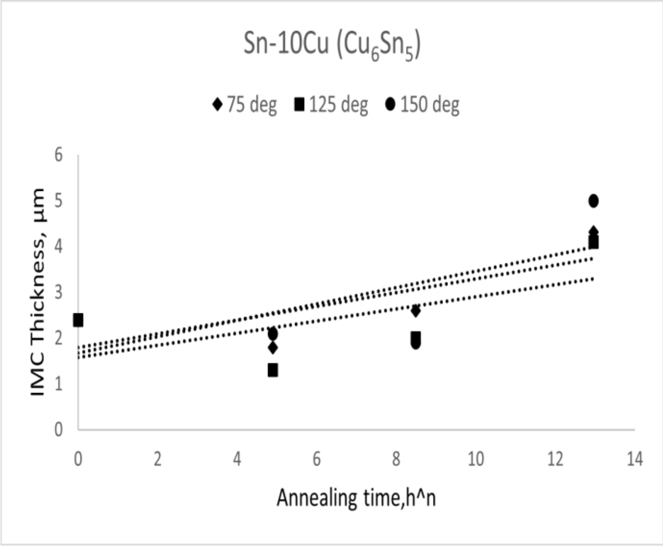

Figure 13. Cu_6Sn_5 IMC thickness versus aging time for Sn-10 wt.% Cu.

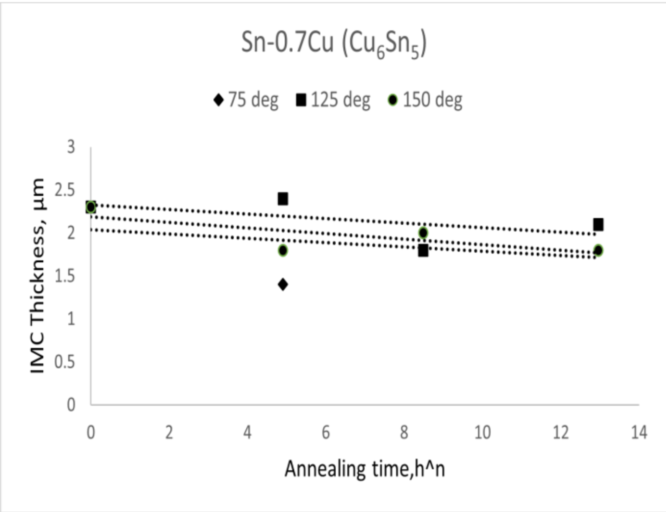

Figure 14. Cu_6Sn_5 IMC thickness versus aging time for Sn-0.7 wt.% Cu.

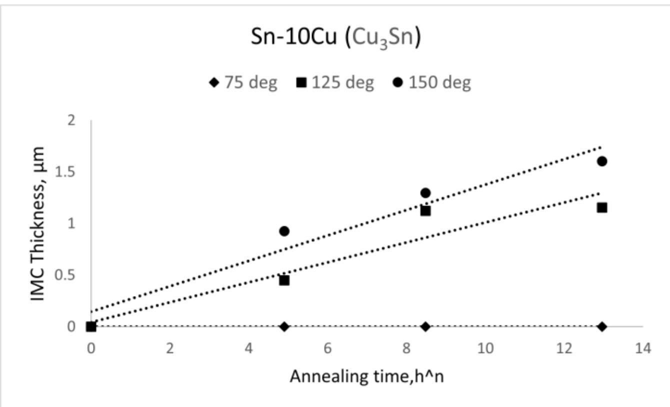

Figure 15. Cu_3Sn IMC thickness versus aging time for Sn-10 wt.% Cu.

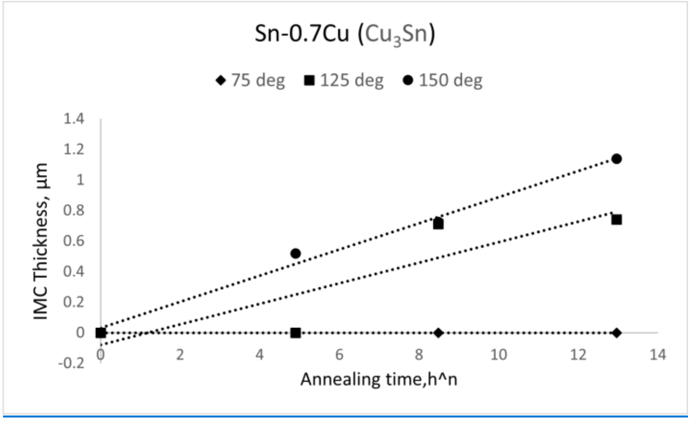

Figure 16. Cu_3Sn_5 IMC thickness versus aging time for Sn-0.7 wt.% Cu.

The calculated Arrhenius plot is shown in Figure 17, and the activation energies were estimated from the slope of the Arrhenius plot. The values for the solder joints for Sn-10 wt. % Cu and Sn-0.7 wt. % Cu are 22.44 and 31.20 kJ/mol, respectively. It was found that the activation energy of Sn-0.7 wt. % Cu solder is higher compared to Sn-10 wt. % Cu solder. Generally, the activation energy is defined as the minimum energy required for the reaction to occur. A higher activation energy of the solder leads to higher thermodynamic stability of the reaction [13]. Previous studies have found that the activation energy for the Sn-10 wt. % Cu solder joint/Cu substrate has been calculated at around 26.76 kJ/mol [14]. Thus, the activation energy found in this study is nearly consistent with the previous findings.

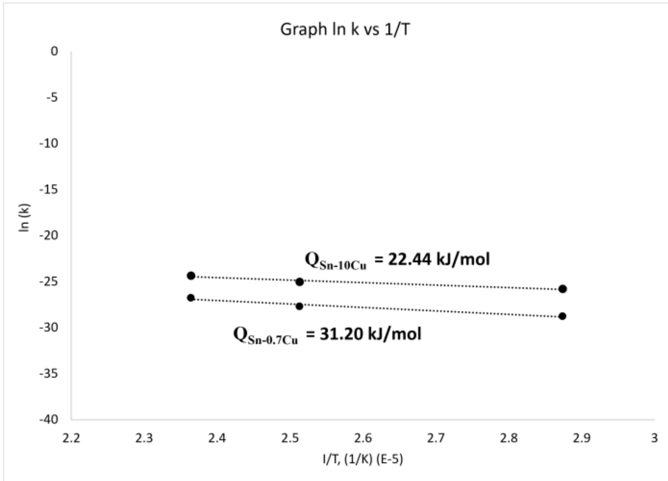

Figure 17. Arrhenius plots for the growth of the IMC layer at Sn-10wt. % Cu and Sn-0.7 wt. % Cu solder joints

4. CONCLUSIONS

This work concentrated on studying the microstructure evolution of the intermetallic compound (IMC) layer and the activation energy of the Sn-10 wt.% Cu and Sn-0.7 wt.% Cu solder joint on Cu substrate subjected to isothermal aging. The conclusions made from the findings are briefly outlined:

i. Significant IMC growth was seen in the solder joints that had undergone isothermal aging. The two primary IMC layers (Cu_3Sn and Cu_6Sn_5) thickened as the temperature increased.

ii. The microstructure of the solder joints is generally composed of β-Sn and Cu_6Sn_5 / β-Sn eutectic composition. With an increasing aging temperature, the Cu_3Sn phase disintegrates which allows the Cu_6Sn_5 to grow rapidly.

iii. The growth rate of the solder joints increased with increasing temperature. Overall, the Sn-0.7 wt.% Cu solder joint possessed higher activation energy (31.20 kJ/mol) compared to the Sn-10 % Cu solder joint which had an activation energy of 22.44 kJ/mol.

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