Effects of copper content in Sn-based solder on the intermetallic phase formation and growth during soldering

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Abstract. This research has studied the effects of copper contents in the Sn-based solder (i.e. Sn-0.7Cu, Sn-1.0Cu, and Sn-3.0Cu) on the intermetallic phase formation and the growth during soldering. In the experiments, reflow soldering was performed at 350 °C with the Cu substrate by using three solders for various soldering times of 10, 20, 40, 60, 120, 240 and 480 s. XRD data have shown that the η-Cu₆Sn₅ and ε-Cu₃Sn phases with hexagonal crystal structure were present between the solder and the substrate. The presence of ε-Cu₃Sn phase was found only when the substrate was soldered for at least 240 s. The Cu content in solder had significant effects on the intermetallic growth with long term soldering time. In addition, the diffusion coefficient was correlated to the Cu content in the solder.

1. Introduction
Copper (Cu) is widely used as an electrical conductor in circuit boards, due to its high electrical and thermal conductivity [1]. Solder alloy is used to connect the electronic devices onto the Cu substrate. Among tin (Sn)-based solder systems, the Sn–Cu solder is considered as the most promising candidate to replace the Sn-Pb solder compared to other solders because of their low melting temperature and favorable properties [2]. In soldering processes, where a solder is in contact with a Cu substrate, there are phenomena involving the development of a nucleus and the subsequent formation and the growth of intermetallic compound (IMC). Hence, the reaction between the Cu and Sn components in an equilibrium state induces the IMC beginning to form at the interface of the solder and substrate [3, 4].

It is well known that the Cu-Sn soldering system has two interfacial phases which are Cu₆Sn₅ and Cu₃Sn phases [5]. At lower temperatures, the crystal phase of Cu₆Sn₅ is monoclinic. However, this η’-Cu₆Sn₅ phase can transform to hexagonal η-Cu₆Sn₅ phase with higher temperature [6]. The η-Cu₆Sn₅ phase transforms from the hexagonal to monoclinic during the cooling procedure. In terms of ε-Cu₃Sn phase, the crystal structure is a hexagonal sphere packing with A₃ structure type [7]. Besides, there are phase transitions from A₃ structure to D₀₁₉ structure during quenching process from high temperature. Furthermore, the ε-Cu₃Sn phase has an orthorhombic structure which develops during the solidification process of the Cu–Sn alloy. As the ε-Cu₃Sn phase is often described as an orthorhombic crystal system due to orthorhombic unit cell, and thus constitutes to the hexagonal structure [7, 8].

The microstructure and reaction interface changes were influenced by increasing the ratio of Cu to solder [9]. Higher Cu compositions in the solder assist the formation and increase the growth of Cu₆Sn₅ instantly [10, 11]. Typically, IMCs are less ductile which is related to their low thermal and low electrical conductivity. The low ductility (i.e. brittleness) of the IMCs contributes to the fatigue.
lifetime reduction of solder joints. In other words, the presence the growth of IMCs has an impact on the reliability of solder joints [12, 13]. Nonetheless, the formation and growth of IMC at the interface are influenced by various factors, including the Sn content and reflow conditions [14]. Despite several studies on the concentration of the Cu in the solder, the effects of a higher concentration of Cu in the solder have not been shown, especially with 3.0 wt.% of Cu in the Sn-based solder. The aim of this study is to investigate the effects of Cu contents in the Sn-based solder on the IMC formation and the growth during reflow soldering.

2. Experiment

2.1. Materials and methods

The experiments were carried out using Sn-based solder with 0.7, 1.0 and 3.0 wt% of Cu, termed Sn-0.7Cu, Sn-1.0Cu and Sn-3.0Cu respectively. The solder bar was casted to have a diameter of 6.5 mm and a thickness of 1.24 mm (JIS Z3198-3). The Cu substrates with purity of 99.99% (JIS H3100) were 0.2 mm thick and 25×30 mm. Prior to reflow soldering, the substrate was cleaned using dilute HCl acid and flux (RC-15SH RMA (15%)) was droplets onto the substrate. For the soldering process, the substrate was placed onto a hot plate followed by the solder. Next, the temperature was increased to 350 °C for 10, 20, 40, 60, 120, 240 and 480 s respectively. After soldering, samples were mounted and polished respectively. The polished surface was etched with a solution containing of 93% ethanol, 5% nitric acid and 2% HCl. Samples were then analysed with the following techniques. Firstly, scanning electron microscopy (SEM, JEOL; JSM-5800LV) was used to verify the microstructure and intermetallic phases. Secondly, an energy dispersive spectroscopy (EDS, OXFORD INSTRUMENTS, X-Max) was used to determine the chemical compositions of the IMCs. Finally, X-ray diffraction (XRD, Bruker, D8-Discover) was carried out to analyze the crystal and lattice structure parameters of IMCs.

3. Results and Discussion

3.1. Intermetallic phase formed during soldering

During reflow soldering, the Cu substrate is in contact with solder bringing about the prediction of the IMCs generated from the Sn-Cu binary phase diagram. As a result, two intermetallic layers which are Cu$_6$Sn$_5$ and Cu$_3$Sn phase are clearly visible at the temperature of 350 °C in the soldering process while other Cu-Sn IMCs, such as Cu$_{10}$Sn$_3$ and Cu$_{41}$Sn$_{11}$, are found at the higher temperature [6]. The IMCs of Cu$_6$Sn$_5$ and Cu$_3$Sn were introduced by the reaction between the Sn atoms from the solder and Cu atoms from the substrate [15, 16] which can be explained by Equations (1)-(2):

$$\begin{align*}
6\text{Cu} + 5\text{Sn} & \rightarrow \text{Cu}_6\text{Sn}_5 \\
3\text{Cu} + \text{Sn} & \rightarrow \text{Cu}_3\text{Sn}
\end{align*}$$

The diffusion of atomic species, Sn and Cu passing through the interface results in the formation of the first Cu$_6$Sn$_5$ layer followed by the Cu$_3$Sn layer adjacent to the Cu substrate [17]. Meanwhile, the Cu$_3$Sn could react with Sn atoms to form Cu$_6$Sn$_5$ [18]. According to Equation (3), Sn is released in liquid state. However, it was reported that Cu$_6$Sn$_5$, which is a kinetically favorable phase, is unstable with Cu, but Cu$_3$Sn, as a thermodynamically steady phase, is stable with Cu. Thus, if there is free Cu in the system, Cu$_3$Sn$_5$ tends to decompose. This can occur by two ways, either by adding Cu or by subtracting Sn from Cu$_6$Sn$_5$. The chemical reactions converting Cu$_6$Sn$_5$ to Cu$_3$Sn are shown in Equations (4)-(5) [18, 19].

$$2\text{Cu}_3\text{Sn} + 3\text{Sn} \rightarrow \text{Cu}_6\text{Sn}_5$$

$$\ldots$$
Cu₆Sn₅ + 9Cu → 5Cu₃Sn
Cu₆Sn₅ → 5Cu₃Sn + 3Sn

Nevertheless, addition of Cu by Equation (4) results in a Cu₆Sn₅ layer between the Cu₆Sn₅ layer and the Cu substrate where the Cu atom refers to the dissolved substrate [20]. Thus, η-Cu₆Sn₅ forms first and ε-Cu₃Sn forms later at the η-Cu₆Sn₅/Cu interface. In the aspect of the depletion of Sn from η-Cu₆Sn₅ in Equation (5), the Sn tends to diffuse to the side of Cu to form ε-Cu₃Sn. However, there must be a sink for Sn or the presence of a nearby Cu to attract Sn. From previous research, many phenomena occurred which were related to the ε-Cu₃Sn and associated with the size of the IMC. Thus, we shall discuss and conclude with the thickness of IMC details.

The SEM observation was carried out to study the formation of IMCs at various soldering times and solder compositions as shown in Figure 1. In the experiment, similar IMC formation was found between solder and Cu substrate. Two types of IMCs (η-Cu₆Sn₅ and ε-Cu₃Sn) were found at the interface. However, ε-Cu₃Sn was found only when the Cu substrate has been soldered for longer soldering times (240 s and 480 s), while η-Cu₆Sn₅ was found at other soldering conditions (10 s - 120 s).

Figure 1. IMCs found at various soldering conditions.

The chemical composition of both IMCs was determined via EDS analysis as illustrated in Figure 2. The findings indicated that Cu contents of the η-Cu₆Sn₅ phase range from 51.11 at.% to 52.77 at.%, the region of ε-Cu₃Sn an elemental content of 70.74 at.% to 73.38 at.% Cu and respective Sn is found. The confirmation of phase formation was determined via XRD analysis as illustrated in Figure 3. From the XRD pattern of the specimen, the Cu phase is α-Cu which consists of a face-centered cubic structure, and the solder is β-Sn which adopts a body centered tetragonal structure. The crystal structure of both η-Cu₆Sn₅ and ε-Cu₃Sn is hexagonal. The a, b and c lattice parameters of η-Cu₆Sn₅ were 4.200, 4.200 and 5.090 angstrom. The η-Cu₆Sn₅ phase conforms to a B81 structure and a space group of P63/mmc. The lattice parameters of ε-Cu₃Sn displays the a and b were 2.749 and 4.322 angstrom respectively. However, η-Cu₆Sn₅ did not transform to η′-Cu₆Sn₅ during the cooling period of the reflow.
3.2. Thickness of intermetallic compound

The thickness of IMCs at different soldering conditions was also examined, the results are shown in Figure 4. The findings indicated that with a soldering time of 10 s there is no difference in the thickness of \( \eta \)-Cu\(_6\)Sn\(_5\) layer, Figure 4 (a). Due to the short soldering time, the supply of Cu and Sn atoms to their corresponding interfaces was composed of two parts, released from substrate or solder, and the decomposition of IMC phase. Following soldering at 20–40 s, the thickness of the IMC of both solders between Sn-0.7Cu and Sn-1.0Cu were not different, since both solders have slightly different Cu compositions. In contrast, the thickness behavior of Sn-3.0Cu solder was different, the thickness of \( \eta \)-Cu\(_6\)Sn\(_5\) at the interface was significantly higher than those in the Sn-0.7Cu/Cu and Sn-1.0Cu/Cu. As the soldering time extended from 60 s to 120 s, the IMC thickness increased as a function of reflow time and Cu content. The Cu atoms can also diffuse from the substrate into solder through the intermetallic layer, and then react with Sn atoms to form huge Cu\(_6\)Sn\(_5\) precipitates within the solder matrix. However, Cu atoms from substrate and solder not only reacted with Sn atoms diffused to promote the continuous growth of \( \eta \)-Cu\(_6\)Sn\(_5\) layer [21]. Nevertheless, evidence of the transition from \( \eta \)-Cu\(_6\)Sn\(_5\) to \( \varepsilon \)-Cu\(_3\)Sn according to Equation (4) was not found.

At a soldering time of 240 s, \( \eta \)-Cu\(_6\)Sn\(_5\) tends to decompose, indicated by a reduced thickness of the \( \eta \)-Cu\(_6\)Sn\(_5\). The Sn could diffuse through the \( \eta \)-Cu\(_6\)Sn\(_5\) to react with Cu, it formed the \( \varepsilon \)-Cu\(_3\)Sn phase. Moreover, \( \eta \)-Cu\(_6\)Sn\(_5\) tended to decompose due to subtracting Sn from \( \eta \)-Cu\(_6\)Sn\(_5\), as illustrated by Equation (5). Thus, experiments have found that \( \eta \)-Cu\(_6\)Sn\(_5\) forms firstly and is followed by \( \varepsilon \)-Cu\(_3\)Sn at the \( \eta \)-Cu\(_6\)Sn\(_5\)/Cu interface after a certain period of soldering. Figure 4 (b) illustrate the thicknesses of \( \varepsilon \)-Cu\(_3\)Sn layers when soldered at 240 and 480 s. The \( \varepsilon \)-Cu\(_3\)Sn thickness tended to increase with the expansion of the Cu content and soldering time. In addition, Cu is the dominant diffusing species in the \( \varepsilon \)-Cu\(_3\)Sn layer. Therefore, Cu atoms diffuse through the \( \varepsilon \)-Cu\(_3\)Sn layer and react with the existing \( \eta \)-Cu\(_6\)Sn\(_5\) to form the \( \varepsilon \)-Cu\(_3\)Sn growth, as expressed in Equation (4). Thus, the formation and growth of \( \varepsilon \)-Cu\(_3\)Sn agrees with Equations (5) and (4) respectively. In addition, the \( \varepsilon \)-Cu\(_3\)Sn will grow at the
expense of the η-Cu₆Sn₅ phase. The total thickness of the intermetallic layer is the sum of the thicknesses of ε-Cu₆Sn and η-Cu₆Sn₅ layers as shown in Figure 4 (c). The enhancement in the thickness of one phase proportionally reduces the thickness of the other phases in order; consequently, the growths of η-Cu₆Sn₅ and ε-Cu₆Sn are interrelated.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Thickness of IMCs: (a) η-Cu₆Sn₅, (b) ε-Cu₆Sn, and (c) η-Cu₆Sn₅ + ε-Cu₆Sn.

### 3.3. Calculation of diffusion coefficients

The growth of the intermetallic compounds during soldering condition can be expressed by the Equation:

\[ Y = Y_o + \sqrt{Dt} \]

where \(Y_o\) is the thickness of the intermetallic compound at \(t = 0\), \(D\) is the diffusion coefficient. The value of \(D^{1/2}\) could be determined from the slope of plot between the thickness of the intermetallic layer \((Y)\) and the square root of soldering time \((t^{1/2})\).

Table 1 presents the comparison of the effective diffusion coefficients of the IMCs for Sn-0.7Cu/Cu, Sn-1.0Cu/Cu and Sn-3.0Cu/Cu solder joints. It was observed that the diffusion coefficient was correlated to the Cu content in the solder. Since the diffusion coefficients for the ε-Cu₆Sn of this study were higher than the η-Cu₆Sn₅. Due to the formation and growth of ε-Cu₆Sn phase is the sum of the product of Equations (4) and (5), and ε-Cu₆Sn phase increases in thickness at the expense of η-Cu₆Sn₅ phase.

| Solder  | Cu₆Sn₅ (µm²/s) | Cu₆Sn (µm²/s) |
|---------|---------------|---------------|
| Sn-0.7Cu| 0.15340       | 0.370         |
| Sn-1.0Cu| 0.20410       | 0.395         |
| Sn-3.0Cu| 0.40785       | 1.010         |

The finding indicates that the intermetallic phase is fast for the formation and growth with increment of Cu content in solder. The higher Cu content of solder promotes Cu diffusion flux in bulk solder, and promotes nucleation of the interface. Nucleation of the interface can come from both new combination and pre-existing clusters to form IMC [22]. Moreover, the η-Cu₆Sn₅ growth at the solder/η-Cu₆Sn₅ interface was promoted due to the larger amount and size of Cu-Sn clusters. In summary, this study demonstrates the effects of differences in Cu content on the growth of IMC, which can be used as a guide for the selection of solder alloys in Sn-based solder.

### 4. Conclusions

This research studied the effects of Cu content in the Sn-base solder on the formation and growth of IMCs. XRD results showed η-Cu₆Sn₅ phase forms first followed by ε-Cu₆Sn at the η-Cu₆Sn₅/Cu interface. As soldering time increased from 240 s to 480 s, the intermetallic phase of the joint transformed from a single η-Cu₆Sn₅ phase to coexisting η-Cu₆Sn₅ and ε-Cu₆Sn phase. However, the Cu content in the solder had significant effects on the IMC growth with the long-term soldering time. The diffusion coefficient was correlated to the Cu content in the solder. The diffusion coefficient of the solder joints is high when the Cu content in the solder increases.
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Acknowledgements
The authors would like to express sincere gratitude to King Mongkut’s Institute of Technology Ladkrabang (KMITL)’s Faculty of Engineering for the financial support.