Evaluation of Alloying Additions on the Microstructure and IMC Formation of Sn-Ag-Cu Solder on Cu and Ni (P) Substrates

S.O. Shazlin and M.S. Nurulakmal

Abstract—Studies have shown that the SnAgCu solder family has been widely used as a replacement for conventional Sn-Pb solders. An attractive approach is by introducing alloying additives (rare earth elements (RE), Zn, Co, Fe, Ni, Sb) into the SnAgCu solder, which helps in refining the microstructure also improving the mechanical and wetting properties of the solder. The present work focuses on the effect of additions of 0.5% Ce and Fe into Sn-3.0Ag-0.5Cu solder, in attempt to reduce the intermetallic compound (IMC) growth and reflow properties of the solder on Cu and Ni (P) surface finish, as well as effects thermal aging on the formation of intermetallic compound (IMC) on different surface finish. Excessive intermetallic compound growth may effect the interface and solder joint due to the brittle nature of the intermetallic compounds. Thus, by introducing alloying elements, IMC layer thickness can be decrease, resulting in better joint and solder reliability.

Keywords—Alloying Elements, Cu and Ni (P) Substrate, Intermetallic Compound (IMC), Reflow, Thermal Aging.

I. INTRODUCTION

In electronics packaging, solder interconnection plays an important role in providing electrical connections as well as the sole mechanical attachment of the electronic component to the printed circuit board (PCB) [1]. However, waste from electrical and electronic equipment (WEEE) and restriction of the use of certain hazardous substances (RoHS) legislation in Europe were issued that aimed to prohibit the use of Sn-Pb solders due to concern over toxicity of Pb in Sn-Pb solders [2]. The substrate used was bare Cu as well as Ni-P on coating Cu. Molten solder was then casted into flat round shape and cut to small disk for reflow and used zinc chloride as flux. Reflow was done at 3 different temperatures 220°C, 230°C and 240°C for 30 seconds. Then, the samples were cooled to room temperature and prepared for observations on the cross section of IMC formed at the interface. Half of the samples obtained were then thermally aged in the oven at 150°C for 500 hours.

The microstructures and chemical compositions were observed with a scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX). Also, the compositions of the phases formed at the interface were determined. Several micrographs were taken in different areas along the IMCs formed at the solder joints. The thickness of the intermetallic layer was measured to compare the effects of alloying elemental addition, reflow temperatures as well as thermal aging on the intermetallic compound formation between the solder and substrate.

III. RESULTS AND DISCUSSION

The effect of alloying elements (0.5 wt% Ce and 0.5 wt% Fe) on the intermetallic compound (IMC) formed between the solder joint is studied. To provide a baseline for this comparison, the characteristic results included that of for Sn-3.0Ag-0.5Cu alloy.

A. IMC of solders on Cu substrates

Fig. 1 shows SEM image of the interface observed between Sn-3.0Ag-0.5Cu solder alloy on Cu substrate. The reaction layer formed between the solder and substrate is the scallop-type Cu6Sn5, consistent with that of reported in the literatures [5]–[8]. As the reflow temperature increases, the thickness of the intermetallic layer Cu6Sn5 increases and the shape changes from scallop-type to elongated scallops, as seen in Fig. 1 (a)–
When the temperature is increased, the diffusion of Cu into Sn is faster, resulting in the increase in the intermetallic compound (IMC) thickness.

Fig. 2 shows SEM image of the interface observed between solder and substrate when alloying elements Ce and Fe are added. The reaction layer that formed was planar scallops, as compared to the intermetallic layer of Sn-3.0Ag-0.5Cu solder, which were rounded scallops. However, as the reflow temperature increases the intermetallic layer becomes thicker and more elongated, as seen in Fig. 2 (a)–(c).

It was mentioned in literatures [9]–[11] that rare earth elements (RE) are known to be the vitamins of metals, whereby a small amount of rare earth elements may change its properties such as refining the microstructure. However, small addition of Fe may increase the intermetallic thickness, as in [12]. In this paper, the addition of Ce and Fe was found to be similar to the results obtained by the literatures [9]–[12]. Although Ce and Fe did not affect the reaction product, which was $\text{Cu}_6\text{Sn}_5$, they did affect the growth of $\text{Cu}_6\text{Sn}_5$. The thickness of the intermetallic compound layer with the additions of Ce and Fe increased, but with more refined planar scallops.

Table 3 shows the thickness of intermetallic compound (IMC) layer of both solders, with the increasing reflow temperature. With the addition of Ce and Fe, the thickness increases slightly as compared to Sn-3.0Ag-0.5Cu solder. As the reflow temperature increases, both the solder exhibit the same increasing growth.

<table>
<thead>
<tr>
<th>Solder</th>
<th>IMC Thickness (μm)</th>
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<tbody>
<tr>
<td></td>
<td>220°C</td>
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<tr>
<td>Sn-3.0Ag-0.5Cu</td>
<td>3.84</td>
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<tr>
<td>SAC-0.5Ce-0.5Fe</td>
<td>4.07</td>
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SAC = Sn-3.0Ag-0.5Cu

B. IMC of solders on Ni (P) substrates

Fig. 4 shows the SEM image of the interface observed between solder and substrate of Sn-3.0Ag-0.5Cu solder on Ni (P) substrate. The intermetallic compound layer observed was $\text{Ni}_3\text{Sn}_4$ scallop-type. Ni from the Ni (P) coating acts as a diffusion barrier between Sn and Cu.

With the increase in reflow temperature the intermetallic compound layer grows and becomes thicker and chunkier, as seen in Fig. 4 (a)–(c).

As the alloying elements Ce and Fe were added, the intermetallic compound (IMC) layer formed at the interface becomes refined (Fig. 5). However, the thickness of the intermetallic compound (IMC) layer formed was decreased, as compared to the Sn-3.0Ag-0.5Cu solder. Table 6 shows the difference in the intermetallic compound (IMC) layer thickness of both solders on Ni (P) substrate. It was observed that, with the addition of alloying elements Ce and Fe, the thickness of the intermetallic compound (IMC) layer formed was decreased,
however with the increasing reflow temperatures, the intermetallic compound (IMC) layer continues to grow, as seen in Fig 5 (a)–(c).

With the addition of alloying elements Ce and Fe, the concentration of Sn reduces, resulting in low diffusion of Sn. The primary growth of intermetallic compound (IMC) layer is controlled by the diffusion of Sn. When the alloying elements are added, the diffusion rate of Sn in reduced, all together reducing the thickness of the Ni$_3$Sn$_4$ intermetallic compound (IMC) layer formed at the solder/substrate interface.

**C. Effect of Thermal Aging**

Fig. 7 (a)–(c) and Fig. 8 (a)–(c) shows the intermetallic compound (IMC) layer of Sn-3.0Ag-0.5Cu solder and solder with alloying elements Ce and Fe on Cu substrate at 3 different reflow temperatures after thermal aging at 150°C for 100 hours. It was observed that the thickness of the intermetallic compound (IMC) layer increases after thermal aging. Table 9 shows the thickness of the intermetallic compound (IMC) layer after thermal aging.

Two significant layers were observed, Cu$_3$Sn and Cu$_6$Sn$_5$. After thermal aging for 100 hours, Cu$_3$Sn forms a flat layer on the surface of Cu, and Cu$_6$Sn$_5$ continues to grow. The total intermetallic compound (IMC) region (Cu$_3$Sn+Cu$_6$Sn$_5$) increases significantly.

Fig. 9 (a)–(c) and Fig. 10 (a)–(c) shows the intermetallic compound (IMC) layer of both solders at 3 different reflow temperatures on Ni (P) substrate after thermal aging at 150°C for 100 hours. The thickness of the intermetallic compound (IMC) layer is tabulated in Table 11.

After thermally aged for 100 hours, Ni$_3$Sn layer changes to thick chunky (Cu, Ni)$_3$Sn$_5$ layer. Cu diffuses out from the Cu surface to the Ni$_3$Sn$_4$/Ni-Sn-P interface to form (Cu, Ni)$_3$Sn$_5$ due to the reaction with Ni$_3$Sn$_4$ [13]. Ni$_3$Sn$_4$ with low Cu content forms at the beginning of the reaction between solder and substrate, whereas (Cu, Ni)$_3$Sn$_5$ with high Cu content forms after thermal aging due to the continuous supply of Cu. Hence explaining the probability of the transformation of Ni$_3$Sn$_4$ to (Cu, Ni)$_3$Sn$_5$ after thermal aging.
Fig. 7 SEM Backscattered electron micrographs illustrating the solder Sn-3.0Ag-0.5Cu on Cu substrate after reflow at (a) 220°C, (b) 230°C, and (c) 240°C respectively, after aging at 150°C for 100 hours.

Fig. 8 SEM Backscattered electron micrographs illustrating the solder SAC-Ce-Fe on Cu substrate after reflow at (a) 220°C, (b) 230°C, and (c) 240°C respectively, after aging at 150°C for 100 hours.

Table IX

<table>
<thead>
<tr>
<th>Solder</th>
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<th>230°C</th>
<th>240°C</th>
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<tr>
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<td>4.20</td>
<td>5.93</td>
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SAC = Sn-3.0Ag-0.5Cu

Table XI

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<tr>
<th>Solder</th>
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<th>240°C</th>
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<td>Sn-3.0Ag-0.5Cu</td>
<td>5.80</td>
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<td>SAC-0.5Ce-0.5Fe</td>
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<td>5.74</td>
<td>7.68</td>
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SAC = Sn-3.0Ag-0.5Cu

Fig. 9 SEM Backscattered electron micrographs illustrating the solder Sn-3.0Ag-0.5Cu on Ni (P) substrate after reflow at (a) 220°C, (b) 230°C, and (c) 240°C respectively, after aging at 150°C for 100 hours.
A thin, continuous and uniform intermetallic compound (IMC) layer is an essential requirement for good bonding. The thickness of the intermetallic compound (IMC) layer plays an important role to the reliability of the entire package due to its brittle nature and the tendency to generate structural defects.

The addition of Ce and Fe into the conventional Sn-3.0Ag-0.5Cu solder did not change the type of reaction product with Cu and Ni (P). The reaction product was always Cu$_3$Sn, Cu$_5$Sn$_3$, Ni$_3$Sn$_4$ and (Cu, Ni)$_3$Sn$_5$. However, the additives did affect the thickness of the intermetallic compound (IMC) layer. On Cu substrate, the alloying elements were found to increase the thickness of the intermetallic compound (IMC) layer but were able to refine the morphology of the compound formed. On Ni (P) substrates, the alloying elements were able to reduce the thickness of the intermetallic compound (IMC) layer, with the help of Ni acting as a diffusion barrier between the Cu and Sn, slowing down the intermetallic compound (IMC) formation.

Reflow temperature played an important role in the growth of the intermetallic compound (IMC) layer. As the temperature increases, the intermetallic compound (IMC) layer increases significantly. On the other hand, thermal aging gave more time for the intermetallic compound (IMC) to grow, resulting in thicker layers. However, through thermal aging, the reaction product was different as compared to the as reflowed reaction products. Longer time would permit the growth of different reaction products.

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REFERENCES


S.O. Shazlin is currently a full time master’s research student at School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang. She has a degree in Metallurgical Engineering from Universiti Malaysia Perlis in 2009. Her research of interests includes the study on lead-free solder alloy.