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

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***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 solder, due to concern over toxicity of Pb in Sn-Pb solders [2]. Therefore, the development of lead free solders has bloomed in the electronics industry. Among the various lead-free solders, Sn-Ag-Cu family is regarded as the most promising candidate to replace Sn-Pb solders due to its superior mechanical properties and soldering performance as well as their compatibility with current component.

Furthermore, the excess IMC growth in soldered joints due to high tin and higher reflow temperature affects the reliability of soldered joints [3]. Recently it was discovered that with the addition of alloying elements, properties of Sn-Ag-Cu solder can be further enhanced. Several elements have been selected as alloying elements such as Bi, Ag, Cu, In, Sb, Zn, Ni, Co [4].

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II. EXPERIMANTAL PROCEDURE

The alloying elements examined were Ce and Fe and the amount added was fixed at 0.5wt% each. The solder alloy was placed in a ceramic crucible and melted at 500 ± 1°C for 180 min and reheated at 300± 1°C for 180 min twice to ensure homogeneity of the elements. Molten solder was then casted into flat round shape and cut to small disk for reflow.

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 Cu_6Sn_5, consistent with that of reported in the literatures [5]–[8]. As the reflow temperature increases, the thickness of the intermetallic layer Cu_6Sn_5 increases and the shape changes from scallop-type to elongated scallops, as seen in Fig. 1 (a)–

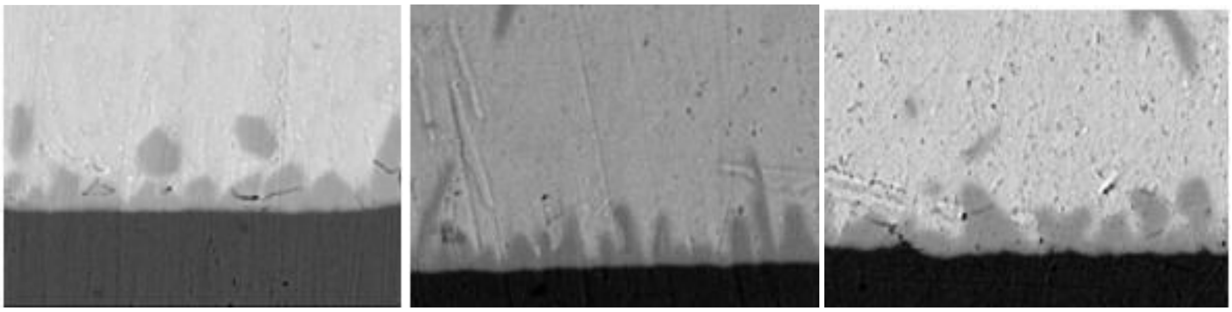

Fig. 1 SEM Backscattered electron micrographs illustrating the solder Sn-3.0Ag-0.5Cu on Cu substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively

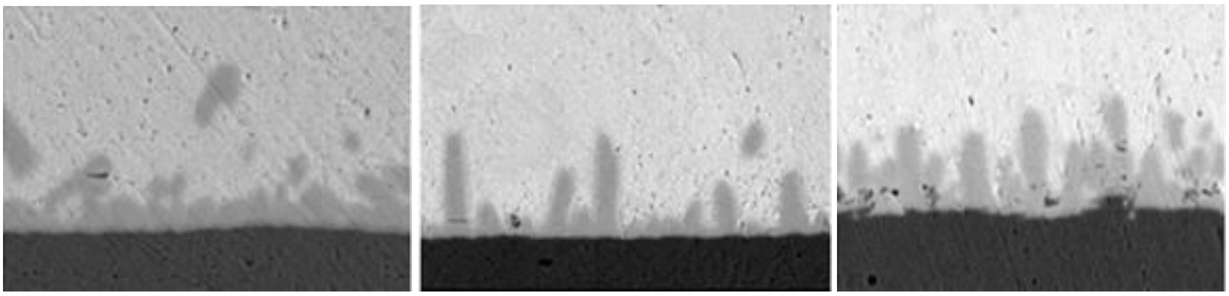

Fig. 2 SEM Backscattered electron micrographs illustrating the solder SAC-Ce-Fe on Cu substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively

(c). 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 Cu_6Sn_5, they did affect the growth of Cu_6Sn_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 III
INTERMETALLIC COMPOUND (IMC) THICKNESS ON CU

Solder	IMC Thickness (μm)		
	220°C	230°C	240°C
Sn-3.0Ag-0.5Cu	3.84	4.99	6.24
SAC-0.5Ce-0.5Fe[1]	4.07	6.14	7.60

[1]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 Ni_3Sn_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,

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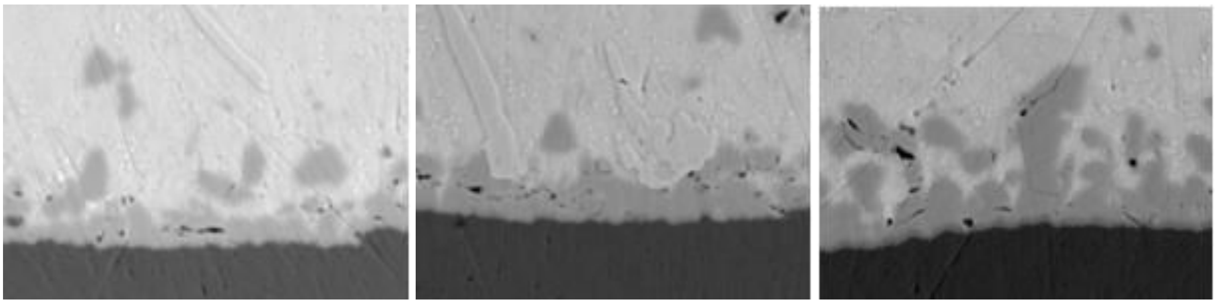

Fig. 4 SEM Backscattered electron micrographs illustrating the solder Sn-3.0Ag-0.5Cu on Ni (P) substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively

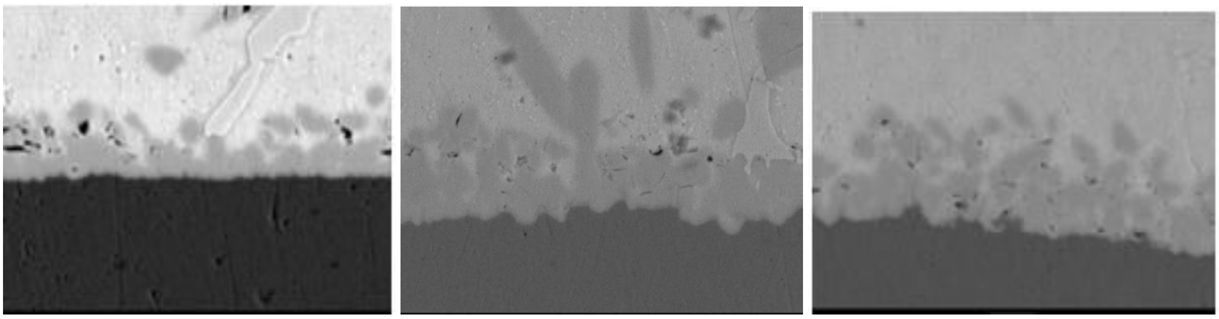

Fig. 5 SEM Backscattered electron micrographs illustrating the solder SAC-Ce-Fe on Ni (P) substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively

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_3Sn_4 intermetallic compound (IMC) layer formed at the solder/substrate interface.

TABLE IV
INTERMETALLIC COMPOUND (IMC) THICKNESS ON NI (P)

Solder	IMC Thickness (μm)		
	220°C	230°C	240°C
Sn-3.0Ag-0.5Cu	4.34	5.93	7.24
SAC-0.5Ce-0.5Fe[1]	4.39	4.88	6.27

[1]SAC = Sn-3.0Ag-0.5Cu

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_3Sn and Cu_6Sn_5. After thermal aging for 100 hours, Cu_3Sn forms a flat layer on the surface of Cu, and Cu_6Sn_5 continues to grow. The total intermetallic compound (IMC) region (Cu_3Sn+Cu_6Sn_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_3Sn layer changes to thick chunky $(Cu, Ni)_6Sn_5$ layer. Cu diffuses out from the Cu surface to the Ni_3Sn_4/Ni-Sn-P interface to form $(Cu, Ni)_6Sn_5$ die to the reaction with Ni_3Sn_4 [13]. Ni_3Sn_4 with low Cu content forms at the beginning of the reaction between solder and substrate, whereas $(Cu, Ni)_6Sn_5$ with high Cu content forms after thermal aging due to the continuous supply of Cu. Hence explaining the probability of the transformation of Ni_3Sn_4 to $(Cu, Ni)_6Sn_5$ after thermal aging.

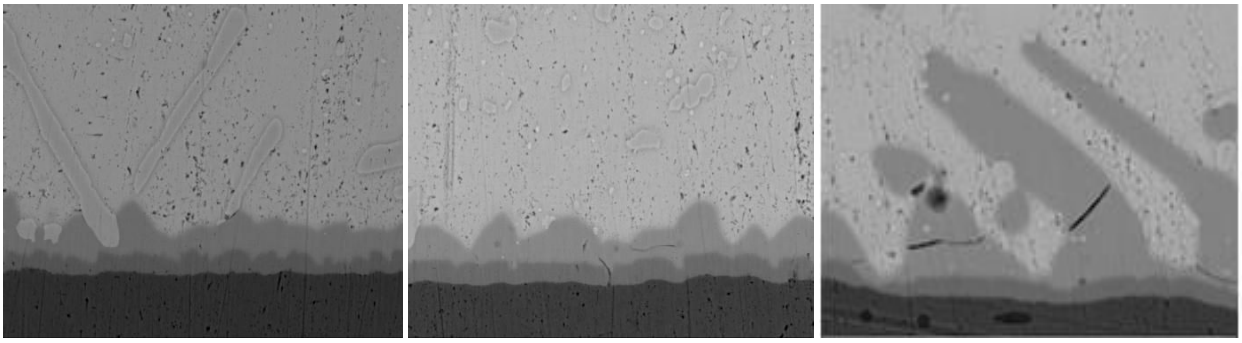

Fig. 7 SEM Backscattered electron micrographs illustrating the solder Sn-3.0Ag-0.5Cu on Cu substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively, after aging at 150°C for 100 hours

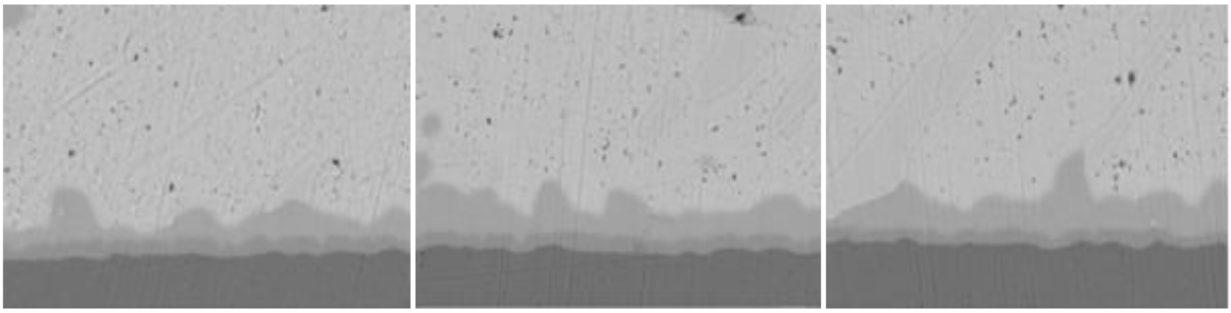

Fig. 8 SEM Backscattered electron micrographs illustrating the solder SAC-Ce-Fe on Cu substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively, after aging at 150°C for 100 hours

TABLE IX
INTERMETALLIC COMPOUND (IMC) THICKNESS ON CU AFTER AGING

Solder	IMC Thickness (µm)		
	220°C	230°C	240°C
Sn-3.0Ag-0.5Cu	4.20	5.93	11.52
SAC-0.5Ce-0.5Fe[1]	4.13	6.43	8.67

[1]SAC = Sn-3.0Ag-0.5Cu

TABLE XI
INTERMETALLIC COMPOUND (IMC) THICKNESS ON NI (P) AFTER AGING

Solder	IMC Thickness (µm)		
	220°C	230°C	240°C
Sn-3.0Ag-0.5Cu	5.80	7.77	9.35
SAC-0.5Ce-0.5Fe[1]	4.90	5.74	7.68

[1]SAC = Sn-3.0Ag-0.5Cu

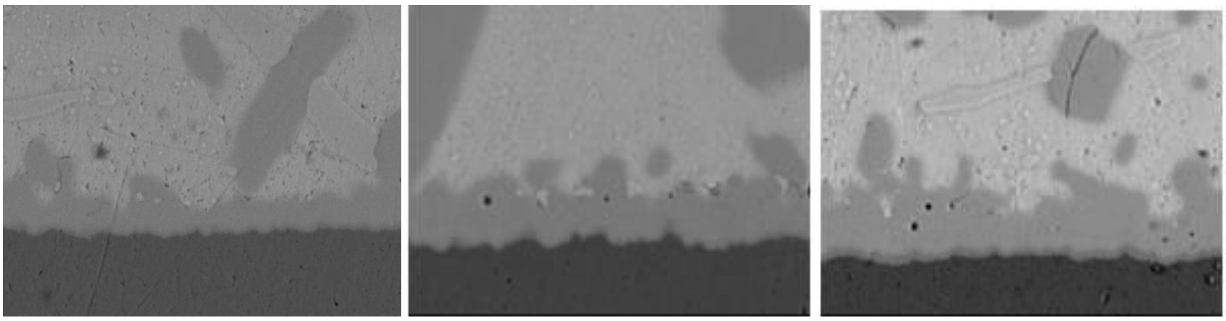

Fig. 9 SEM Backscattered electron micrographs illustrating the solder Sn-3.0Ag-0.5Cu on Ni (P) substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively, after aging at 150°C for 100 hours

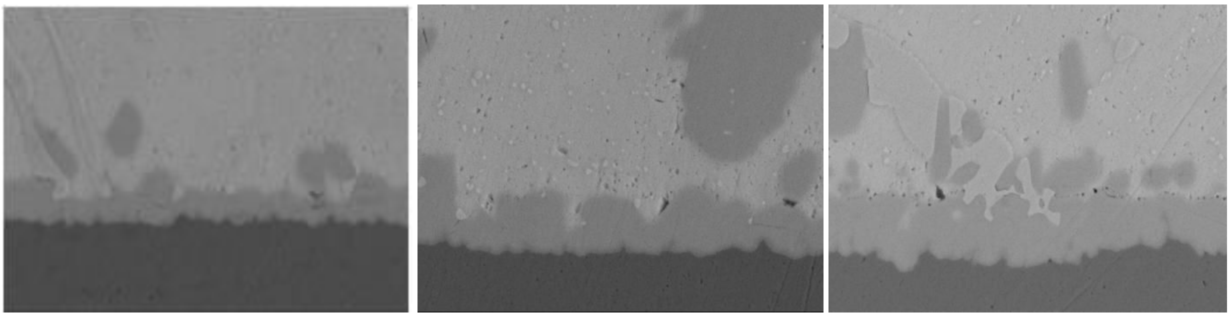

Fig. 10 SEM Backscattered electron micrographs illustrating the solder SAC-Ce-Fe on Ni (P) substrate after reflow at (a) 220°C (b) 230°C and (c) 240°C respectively, after aging at 150°C for 100 hours

IV. CONCLUSION

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_3Sn, Cu_6Sn_5, Ni_3Sn_4 and $(Cu, Ni)_6Sn_5$. 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 product.

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