Interfacial reactions between different Sn-based lead-free solder alloys and CuNi substrates

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Abstract. The effect of the presence of Ni in Cu substrates on the interface reaction during soldering and the growth of Sn-Cu intermetallic compounds (IMCs) was studied. The study involved reflow soldering of Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni lead-free solders on pure Cu and Cu-6Ni substrates with holding times of 5, 10 and 15 minutes at 232 °C. The presence of 6 wt% Ni in the Cu substrate strongly affects the microstructural evolution and the growth of the IMCs. The presence of Ni in the substrate significantly increased the overall thickness of the (Cu,Ni)6Sn5 layer while suppressing the formation of the Cu3Sn layer. The thickness of the (Cu,Ni)6Sn5 layer increased with reflow time for both Cu and Cu-6Ni substrate.

1 Introduction

Recently, there has been interest in the potential to make joints containing high melting point intermetallic compounds (IMCs) by allowing reactions between low melting point materials and high melting point materials with consideration of appropriate pressures and temperatures [1]. These high melting point IMCs are expected to function as reliable interconnection materials operating at high temperature environments and could be suitable for a wide range of applications. One of the methods to form a full IMC is low temperature transient liquid phase (TLP) bonding by interdiffusion between low melting point materials such as tin (Sn) and indium (In) with high melting point materials like copper (Cu), nickel (Ni) and silver (Ag). Due to the high melting temperature of the IMCs, they are thermally stable [2]. Cu5Sn and Cu6Sn5 are brittle IMCs that grow at the interface between Cu substrate and Sn-based solder alloys during the soldering process. These phases grow further by solid-state diffusion and it has been shown that the presence of Ni in the Cu system can greatly influence the growth rate of the Cu5Sn and Cu6Sn5 [3]. It has been reported that addition of Ni in Cu reduces the growth of the Cu5Sn phase and greatly accelerates that of Cu6Sn5 [4-6]. Based on a thermodynamic analysis, the change in Ni content alone is insufficient to explain these changes. An analysis of the IMC growth with respect to the activation energy of the diffusion coefficient also indicates a strong role of grain boundary diffusion in the growth of Cu6Sn5. An analysis of the IMC composition shows the Ni incorporated into the intermetallic, forming (Cu,Ni)6Sn5 during the interfacial reaction between the solder and Cu substrate. This study focuses on the interfacial reaction and thicknesses of the IMCs grown between three

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different solder alloy: Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni with pure Cu and Cu-6 wt% Ni substrates during soldering.

2 Materials and Methodology

2.1 Fabrication of Sn-based solder alloy/Cu-xNi

Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni (herein after referred to as the Sn-based solder alloy) (supplied by Nihon Superior) were used as the solder alloys, while Cu-xNi (x = 0 and 6 wt%) foils were used as the substrates. The Sn-based solder alloys were rolled into sheets with thickness about 100 µm, then cut into dimensions of 10 mm × 10 mm. Cu-xNi foils of 30 - 40 µm in thickness were also cut into the same dimensions. The soldering flux (Pacweld 62) was applied on each Sn-based based solder alloy/ Cu-xNi interface to remove the surface oxides on the Cu-xNi and assist the soldering process. The Sn-based solder alloys were set on the top of the Cu-xNi substrates and clamped between glass slides using metal clips. The heating process of the samples was performed as follow: first, the oven was heated from room temperature to 232°C; second, the prepared samples were placed in the oven and reflowed at 232°C for 5, 10 and 15 minutes; lastly, the reflowed samples were cooled in air. The Sn-based solder alloy/ Cu-xNi couple was then removed from the glass slide and cleaned using acetone to remove the excess flux. The samples were ground with silicon carbide (SiC) paper and then polished with 3 and 1 µm diamond suspension, and final polishing by using oxide polishing suspensions (OPS). The cross-section of the samples was observed using a Hitachi TM3030 scanning electron microscope (SEM). An analysis of the elements present in selected areas was performed using energy dispersive X-ray spectroscopy (EDS). The thickness of the IMCs was measured using image analysis.

3 Result and discussion

3.1 Microstructure evolution of interfacial IMC

Fig 1 shows the interface cross-section of Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni on Cu and Cu-6Ni substrates solder joints reflowed at 232°C for 5 minutes. Previous literature [5, 7, 8] has shown that the (Cu,Ni)6Sn5 intermetallic phase forms and grows faster when Ni is present in the Cu substrate at concentrations between 5 and 10 %. After reflowing for 5 minutes, three IMC morphologies can be observed clearly, namely, a scalloped morphology at the Sn-0.7Cu/Cu interface, a combination of scalloped and columnar morphologies for Sn-3Ag-0.5Cu/Cu and a near-flat and stable IMC growth at the interface of Sn-0.7Cu-0.05Ni/Cu, as seen in Fig 1(a-c). The formation of the scalloped Cu6Sn5 intermetallics is the results of a combination of kinetics processes including ripening and interfacial reactions [5] while the stable formation of the IMC for Sn-0.7Cu-0.05Ni/Cu may be due to the role of Ni in suppressing the polymorphic transformation of Cu6Sn5 [9, 10]. From the cross-section of Sn-0.7Cu/Cu-6Ni, Sn-3Ag-0.5Cu/Cu-6Ni and Sn-0.7Cu-0.05Ni/Cu-6Ni shown in Fig 1(d-f), it is clearly seen that the growth of the IMCs is accelerated and becomes thicker compared to the pure Cu substrate, however the IMCs are no longer continuous and in full contact with the substrate (at least in two dimensions) with the exception of the Sn-0.7Cu-0.05Ni/Cu-6Ni joint. The formation of Cu6Sn5 intermetallics is reliant on the diffusion of Cu from the substrate to the Sn-based solder/Cu interface [2, 11] and this interfacial reaction is accelerated in the case where the substrate contains 6 wt% Ni. The discontinuity of the interfacial IMC
(in the Ni containing substrates and the Sn-0.7Cu and Sn-3Ag-0.5Cu solder alloys) may lead to massive spalling of the Cu-Ni-Sn ternary compounds during growth [5, 8].

As the reflow time increased from 5 to 15 minutes, the Cu$_6$Sn$_5$ intermetallic layer grew thicker with a scalloped morphology and a layer of Cu$_3$Sn formed between the Cu$_6$Sn$_5$ and Cu substrate for Sn-0.7Cu/Cu (see Fig 2(a)), while for Sn-0.7Cu/Cu-6Ni, the formation of (Cu,Ni)$_6$Sn$_5$ intermetallic consumed the Sn-0.7Cu solder entirely (see Fig 2(b)). A reduction of the thickness of the Cu-6Ni substrates also results from the reaction process. For Sn-3Ag-0.5Cu on Cu and Cu-6Ni, Ag$_3$Sn intermetallics were found at the interface above the CuSnNi layer, however due to the thin layers of the intermetallic, it is difficult to quantitatively analyze this phase [8]. An elemental mapping analysis was done to confirm the (Cu,Ni)$_6$Sn$_5$ intermetallic phases formed. From previous reported literature, the Cu$_6$Sn$_5$ compound can extend to ternary compositions due to the presence of Ni forming (Cu,Ni)$_6$Sn$_5$ ternary intermetallic compounds [8, 12, 13]. Similar intermetallic growth was also found for Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni when reflowed on Cu substrates. Addition of Ni atoms are believed to suppress the formation of the Cu$_3$Sn [5] and no trace of Cu$_3$Sn layer was found in Fig 2(b).
3.2 Thickness of IMCs

The relationship between the total interfacial IMC thickness and reflow time for all three Sn-based solders; Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni on Cu and Cu-6Ni substrates are shown in Fig 3. As shown in Fig 3(a), the IMCs on the pure Cu substrate grow continuously throughout the 15 minutes of reflow. When reacting with pure Cu substrate, the thickness of the IMC grew to a maximum of 5 µm with the Sn-3Ag-0.5Cu and this was the highest compared to the other two solders. When 6 wt% of Ni was present into the Cu substrate, the IMC growth accelerated and the maximum thickness was much larger than that present in reactions with the Ni-free substrates. Similar to the example shown in Fig 2(b), the full formation of the IMC was observed at reflow time of 15 minutes for all Sn-based solders on the Cu-6Ni substrate.

![Fig. 3. Total IMC thickness versus the reflow time with Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni solder on different substrate: (a) Cu and (b) Cu-6Ni substrates](image)

4 Conclusion

The effects of having Ni present in the Cu substrate on the interfacial reaction and IMC growth when reacting with Sn-0.7Cu, Sn-3Ag-0.5Cu and Sn-0.7Cu-0.05Ni solders were studied. The following conclusions can be made:

1. With a reflow time of 5 minutes, different morphologies of Cu₆Sn₅ intermetallic formed when three different solders reacted with pure Cu substrates; scalloped IMCs formed in the Sn-0.7Cu/Cu couple, while scalloped and columnar IMCs formed in the Sn-3Ag-0.5Cu/Cu couple and near-planar IMC growth occurred at the interface of the Sn-0.7Cu-0.05Ni/Cu couple. With the presence of 6 wt% Ni in the Cu substrate, when reflowed for 5 minutes, the Cu₆Sn₅ intermetallic growth accelerated significantly for Sn-0.7Cu and Sn-3Ag-0.5Cu while for Sn-0.7Cu-0.05Ni, the Cu₆Sn₅ was slightly thicker compared to Sn-0.7Cu-0.05Ni/Cu.

2. With an increase in the reflow time to 15 minutes, the planar-like Cu₃Sn layers grew between the Cu₆Sn₅ and Cu substrate but when Ni was present in the Cu substrate, the Cu₃Sn layer was not present at the intermetallic/substrate interface.

3. The presence of 6 wt% Ni increased the growth of the Cu₆Sn₅ intermetallic for all Sn-based solder alloys and a complete transformation of the 100 µm solder sheet occurred after 15 minutes of reflow time.
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