A Novel Electronic Packaging Method to Replace High-Temperature Sn-Pb Solders

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The In/Ni/Cu/Ni/In multilayer was prepared by an electroplating method to replace high-temperature Sn-Pb solders that are conventionally used but are very harmful to the environment. This study shows all the sandwich couples that formed the $(\text{Cu,Ni})_6(\text{Sn,In})_5$ and $\text{Cu}_2\text{In}_3\text{Sn}$ phases at the interface. When the solder joint was reflowed at 200°C, a planar layer $(\text{Ni,Cu})_3(\text{Sn,In})_4$ formed near the Ni layer. When the reflowing temperature was increased to 300°C, another planar layer $\text{Cu}_3(\text{Sn,In})$ formed near the Cu substrate. The greater part of the intermetallic compounds in this case were the $(\text{Cu,Ni})_6(\text{Sn,In})_5$ and $\text{Cu}_3(\text{Sn,In})$ phases. The $\text{Cu}_3(\text{Sn,In})$ phase thickness was increased with increasing aging time. The thicker formation of $\text{Cu}_3(\text{Sn,In})$ phase improved the solder-joint strength. The samples reflowed at 300°C exhibited the best mechanical strength, which was 57.6 kg/cm² as reflowed. This In/Ni/Cu/Ni/In multilayer structure is a suitable candidate for high-temperature Pb-free solders.

Key words: In/Ni/Cu/Ni/In multilayer, high-temperature Sn-Pb solders, intermetallic compounds, mechanical strength

INTRODUCTION

High-temperature solders possess the following special properties:¹ a liquidus temperature between 260°C and 400°C, a narrow mushy zone range, a low volume expansion rate in high temperatures, and good mechanical, electrical and conductive performance. Sn-containing 85–97 wt.%Pb solders have been conventionally used as high-temperature solders. For example, the solidus and liquidus temperatures of the Sn-95Pb solder are 300°C and 314°C, respectively. Bulk manufacturing soldering needs to be at high temperature between 300°C and 350°C to maintain good solder-joint stability. For environmental reasons, solders containing Pb are gradually being replaced by Pb-free solders. Pb-free solders have not entirely replaced high-Pb solders, and high Pb-containing solders have not yet been prohibited by the restriction of hazardous substances directive (RoHS). That being

said, environmental developments will probably result in the obsolescence of Sn-Pb solder at some point in the near future. Thus, discovering new materials or new techniques is an urgent issue. Several candidate alloys, such as Au-20Sn, Bi-Ag, Bi-Sn, Sn-Sb, Al-Zn systems, have been proposed as alternative solders to high-temperature solders. However, none of them can fulfill all the requirements to replace high-Pb content solders.^{2–4} The In/Sn/Metal multilayer structure substrate bonded with Pb-free solders has been successfully adopted in electronic packaging.^{5–7} Yan et al. concluded that the In-48Sn solder bonded strongly with a Cu substrate, which was proven by fractures occurring at solders instead of at interfacial regions in shear testing. The In-Sn/Cu interfacial reaction revealed the Cu/In/Sn/Cu joints bonded with the chip at low temperatures formed intermetallic compounds (IMCs), having melting temperature higher than 300°C. This Cu/IMCs/Cu structure strengthens the bonding of the cap and the base.⁶

This study developed a novel idea to replace high-temperature Sn-Pb solders. Because of the high

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electric and thermal conductivities of Cu and the low eutectic temperature of the In-Sn system, a multilayer structure (In/Ni/Cu/Ni/In) was constructed through electroplating. The proposed new multi-layer structure-(In/Ni/Cu/Ni/In) has the potential to replace conventional high-temperature Sn-Pb solders. The solid-liquid inter-diffusion (SLID) technique was applied as a connection medium. The SLID technique can be used to connect the low-temperature solder and the high-temperature metallic substrate.^{7,8} This In/Ni/Cu/Ni/In multi-layer structure is projected to match the qualities of high-temperature Sn-Pb solders and could therefore replace them.

EXPERIMENTAL

Two different sizes of copper were prepared. One thick copper plate (with an area of 1 cm² and thickness of 1 mm) was first electroplated with one layer of Sn with a thickness of 10 μ m. Another thin copper plate (with an area of 0.5 cm² and thickness of 50 μ m) was also electroplated with one layer of 5 μ m Ni, followed by electroplating one layer of

10 μ m In. The commercial electroplating solution (ST-380) was used, and copper plates were electroplated at an electric density of 7.5 A/dm² in 2 min, 5.0 A/dm² in 2 min and 6.0 A/dm² in 5 min for the Sn, Ni and In layers, respectively. The electroplated copper plates were dipped into rosin mildly activated (RMA) flux and then assembled together as shown in Fig. 1. Then, the assembled solder point samples were aged in a furnace under an air atmosphere without an extra bond force at 200°C, 240°C, and 300°C for 2 h. These reflowing times were commercial operating parameters suggested by Actron Technology Corporation.

After reflowing, all samples were then aged at 100°C for 50–1500 h. After aging, samples were mounted, ground and polished for the IMC examination and identification. Meanwhile, the mechanical shear strength was determined. An electron probe x-ray microanalyzer (EPMA; JEOL JXA-8200; Japan) was used to observe and analyze the IMC composition. The IMC phase was determined by comparison with related phase-diagram databases. A universal testing machine (Shimadzu AI-GS; Japan) was used with a testing speed of 1 mm/min

Fig. 1. Schematics of soldering for the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich structure.

Fig. 2. BEI micrographs of the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple reflowed at (a) 200°C, (b) 240°C and (c) 300°C for 2 h.

to determine the mechanical shear strength. The test did not stop until the samples were broken.

RESULTS AND DISCUSSION

Figure 2a shows the BEI (backscattered electron image) micrograph of this Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple reflowed at 200°C for 2 h. Three different contrast regions can be observed. The compositions of these three layers were determined by using an EPMA, as shown in Fig. 3, which is the EPMA line-scan compositional profile between the Ni and Cu substrates. The gray region has a unique composition of Cu-1.5 at.% Ni-20.4 at.% Sn-21.5 at.% In determined by EPMA analyses. According to the Hume-Rothery rule,⁹ the In and Sn atoms are interchangeable. The Cu-Ni system is an isomorphous system and Cu and Ni atoms have mutual solubility in the Cu-Ni phase diagram.¹⁰ Therefore, the In and Sn atoms were combined to calculate the formed IMC composition, and also for the Cu and Ni atoms. Thus, the gray region is likely the $(\text{Cu,Ni})_6(\text{Sn,In})_5$ phase.¹⁰ In fact, a more detailed analyses and determination for IMC, such as a transmission electron microscopy (TEM) and powder x-ray diffractometer (XRD) analyses should be carried out in the future. However, the EPMA is commonly used to determine the compositions of IMCs and combine the information from the related phase diagrams to identify the IMCs. This method is accepted by most people in the soldering society and the results remain convincing.^{3,5,7,11,12}

The data reveal that a considerable amount of In and Ni atoms are incorporated into the Sn and Cu sublattices of the Cu_6Sn_5 phase. The micro-island shaped and the light region dispersed among the $(\text{Cu,Ni})_6(\text{Sn,In})_5$ phase with a unique Cu-1.0 at.% Ni-14.6 at.% Sn-52.8 at.% In composition is likely the $\text{Cu}_2\text{In}_3\text{Sn}$ phase.^{12–14} According to Lin's report, the $\text{Cu}_2\text{In}_3\text{Sn}$ phase was stabilized at 250°C.¹² The composition of the layer structure region close to the Ni side is Ni-11.3 at.% Cu-29.5 at.% Sn-26.8 at.% In. Koo et al. reported that the layer-shaped $\text{Ni}_3(\text{Sn,In})_4$ phase with the Sn-38.4 at.% Ni-19.1 at.% In composition was formed in the In-48Sn/Au/Ni/Cu couple.¹⁵ However, Wang et al. investigated the interfacial reactions between the molten In-49Sn solder and the Ni substrate. They found that the layer-shaped IMC with the Sn-33.1 at.% Ni-21.4 at.% In composition was formed at the interface and this layer should be the Ni-In-Sn ternary IMC.¹⁶ In comparison with the Ni-Sn binary phase diagram,¹⁰ and Koo and Wang's studies,^{15,16} this continuous layer formed in this study is likely the $(\text{Ni,Cu})_3(\text{Sn,In})_4$ phase, as shown in Fig. 2a.

Figure 2b shows the BEI micrograph of this sandwich reflowed at 240°C for 2 h. According to EPMA line-scan compositional profile as shown in Fig. 3b, these IMCs formed from the Cu to Ni side are the $(\text{Cu,Ni})_6(\text{Sn,In})_5$, $\text{Cu}_2\text{In}_3\text{Sn}$ and $(\text{Cu,Ni})_6(\text{Sn,In})_5$ phases, respectively. As the

Fig. 3. EPMA line-scan compositional profile of the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple reflowed at (a) 200°C, (b) 240°C and (c) 300°C for 2 h.

Fig. 4. BEI micrographs of the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple reflowed at (a) 200°C, (b) 240°C and (c) 300°C for 2 h and aging at 100°C for 1500 h.

Table I. Evolution of IMCs (Cu side to Ni side) in the Cu/Sn/In/Ni/Cu/Ni/InSn/Cu couple reflowed at 200–300°C for 2 h and then aged at 100°C for 50–1000 h

Heat-treatment	Temperature (°C)		
	200	240	300
As reflowing	(Cu,Ni) ₆ (Sn,In) ₅ Cu ₂ In ₃ Sn (Ni,Cu) ₃ (Sn,In) ₄	(Cu,Ni) ₆ (Sn,In) ₅ Cu ₂ In ₃ Sn (Cu,Ni) ₆ (Sn,In) ₅	Cu ₃ (Sn,In) (Cu,Ni) ₆ (Sn,In) ₅ Cu ₂ In ₃ Sn
Aging for 50–1000 h	(Cu,Ni) ₆ (Sn,In) ₅ Cu ₂ In ₃ Sn (Ni,Cu) ₃ (Sn,In) ₄	(Cu,Ni) ₆ (Sn,In) ₅ Cu ₂ In ₃ Sn (Cu,Ni) ₆ (Sn,In) ₅	Cu ₃ (Sn,In) (Cu,Ni) ₆ (Sn,In) ₅ Cu ₂ In ₃ Sn (Cu,Ni) ₆ (Sn,In) ₅

reflowing temperature was increased to 240°C, the Sn layer completely melted and Cu atoms could more easily dissolve into the molten solder then diffuse toward the Ni side. The local Cu concentration on the Ni side would become greater. In this condition, the (Ni,Cu)₃(Sn,In)₄ phase would become unstable and the phase equilibrium condition changed into the two-phase region composed of (L + Cu₆Sn₅). That is why the (Cu,Ni)₆(Sn,In)₅ phase instead of the (Ni,Cu)₃(Sn,In)₄ phase was formed at the Ni side. This result was similar to that in Chen's study.¹⁷ When the Cu concentration became high enough, the phase equilibrium condition would transfer from (L + Ni₃Sn₄) to (L + Cu₆Sn₅) in the Cu-Ni-Sn ternary system.¹⁸ When the reflowing temperature was increased to 300°C, the Cu₃(Sn,In), Cu₂In₃Sn, and (Cu,Ni)₆(Sn,In)₅ phases were found at the interface, as shown in Figs. 2c and 3c. This result was similar to that in the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu couple reflowed at 240°C. Meanwhile, the Cu₃(Sn,In) phase close to the Cu side was observed in this sandwich couple. This result was similar to that in Chuang's study.¹¹ They reported that the Cu₃(Sn,In) phase was formed when the reaction temperature was higher than 300°C. After reflowing, each sandwich couple was then aged at 100°C for 50 h to 1500 h. Figure 4 shows the surface morphologies of these three

sandwich couples reflowed at (a) 200°C, (b) 240°C and (c) 300°C then aged at 100°C for 1500 h. These results indicate that the increase in aging time would not change the types of IMC formation at the interface, but all IMC thicknesses were increased with the increase of aging time.

The evolution of all IMC formation at the interface in the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple as reflowed at 200–300°C and aged at 100°C for various times is listed in Table I. The results indicate that the aged time effect is not significant enough to influence the interfacial reaction but IMC formation is sensitive to the reflowing temperature between the In/Ni/Cu/Ni/In multilayer and Cu-Sn substrate. When the reflowing temperature was raised to 300°C, a new IMC, the Cu₃(Sn,In) phase, was formed at the Cu side and its thickness was increased as the aging time was increased. Meanwhile, the (Ni,Cu)₃(Sn,In)₄ phase disappeared when the reflowing temperature was higher than 200°C.

Figure 5 shows the BEI images of the fracture surface after shear tests for the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couples reflowed at (a) 200°C, (b) 240°C and (c) 300°C for 2 h. As shown in Fig. 5a, only the (Ni,Cu)₃(Sn,In)₄ phase and many dimples are observed at the fracture surface in the sandwich couple reflowed at 200°C. When the reflowing temperature was increased to 300°C, a smooth

Fig. 5. BEI micrographs of the fracture surface after shear tests for the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple reflowed at (a) 200°C, (b) 240°C and (c) 300°C for 2 h.

fractured plane along the fracture surface was observed (Fig. 5c). The fracture type changed from a brittle fracture into a ductile fracture contributed by the thicker $(\text{Cu,Ni})_6(\text{Sn,In})_5$ phase formed at the

Fig. 6. Shear strength of the solder joint in the Cu/Sn/(In/Ni/Cu/Ni/In)/Sn/Cu sandwich couple under different reflow conditions for 2 h at different temperatures (■ 200°C; ● 240°C; ▲ 300°C) and then aged at 100°C for 50–1000 h.

interface. Some In-rich phases with small areas are observed in the matrix in these three samples in Fig. 5. Both Sn and In have a high ductility, thus Sn or In atoms might be spread over the fracture surface after the shear testing. These In-rich phases were not formed at the interface during reflowing.

Figure 6 illustrates the average shear strength of the 24 solder joints in these sandwich couples reflowed at various temperatures for 2 h and then aged at 100°C for 50–1500 h. The shear strength tendency in Fig. 6 decreased when the reflowing temperatures were decreased and aging time increased. Based on Koo's report, the $\text{Ni}_3(\text{Sn,In})_4$ phase formation would reduce the solder-joint shear strength.¹⁶ The $\text{Ni}_3(\text{Sn,In})_4$ phase was only formed when the reflowing temperature was at 200°C. This might be the reason for the deterioration in the shear stress. The lowest shear strength values were always found on the solder joint reflowed at 200°C.

Due to the lesser amount of the $\text{Cu}_2\text{In}_3\text{Sn}$ phase in the sandwich couple reflowed at 300°C, the shear strength value on the solder joints reflowed at 300°C is higher than that reflowed at 200°C or 240°C. The $\text{Ni}_3(\text{Sn,In})_4$ and $\text{Cu}_2\text{In}_3\text{Sn}$ IMCs produce poor solder-joint mechanical strength. The shear strength values of the solder joints in this sandwich couple as reflowed at 300°C and then annealed at 100°C for 1500 h are 57.6 kg/cm² and 37.2 kg/cm², respectively. These results can be compared with the interfacial tensile strength value of 52 kg/cm² from Yan's report,⁶ who tested the Cu/In/Sn/Cu structure bonded at 180°C for 20 min. The result reveals that replacing high-temperature Sn-Pb solders with the (In/Ni/Cu/Ni/In) multilayer solder would be useful in the electronics packaging industry.

CONCLUSIONS

The $(\text{Ni,Cu})_3(\text{Sn,In})_4$, $\text{Cu}_2\text{In}_3\text{Sn}$ and $(\text{Cu,Ni})_6(\text{Sn,In})_5$ phases were formed when the reflowing temperature was at 200°C . When the reflowing temperature was increased to 240°C , the $(\text{Cu,Ni})_6(\text{Sn,In})_5/\text{Cu}_2\text{In}_3\text{Sn}/(\text{Cu,Ni})_6(\text{Sn,In})_5$ structure was observed between the Cu and Ni side. When the sandwich couple was reflowed at 300°C , the $\text{Cu}_3(\text{Sn,In})$, $(\text{Cu,Ni})_6(\text{Sn,In})_5$, $\text{Cu}_2\text{In}_3\text{Sn}$, and $(\text{Cu,Ni})_6(\text{Sn,In})_5$ phases were observed from the Cu to the Ni side. These results indicate that the reflowing temperature has a significant influence on the interfacial reaction between the (In/Ni/Cu/Ni/In) multilayer and the Sn/Cu substrate. The best solder-joint shear strength was obtained in the Cu/Sn/ (In/Ni/Cu/Ni/In) /Sn/Cu sandwich couple reflowed at 300°C . These values were higher than the literature data. This (In/Ni/Cu/Ni/In) multilayer might be suitable for use as a high-temperature Pb-free solder in the electronics packaging industry.

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