Thermal behaviour and microstructural analysis of Sn-0.7Cu alloy and Sn-0.7Cu soldered on electroless nickel/immersion gold

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Abstract. Lead-free solder has been developing since decades due to the environmental and health harmful of lead solder. To compete with the lead solder, the behaviour and properties of lead-free solder have been continually researched and improved. Sn-0.7Cu is one of the most common solder in application and suitable to be used as a control in research. The thermal behaviour by differential scanning calorimeter (DSC) and microstructure formation with elemental analysis by scanning electron microscope (SEM) of Sn-0.7Cu solder alloy was compared to Sn-0.7Cu soldered on electroless nickel/immersion gold (ENIG) substrate in this study. The result showed that the pasty range of Sn-0.7Cu was lower than Sn-0.7Cu/ENIG while the undercooling was higher. Primary and interfacial (Cu,Ni)5Sn5 were formed in Sn-0.7Cu/ENIG due to the diffusion and dissolution of elements from ENIG substrate. The β-Sn dendrites and eutectic phase of Sn-0.7Cu/ENIG was coarser than Sn-0.7Cu due to the decreasing of undercooling.

1 Introduction

The Sn-Pb properties of eutectic composition with low cost, good wettability with low melting point and good in mechanical properties lead to the most preferable material for interconnect in electronic devices. However, lead is one of the toxic material that harmful to the environment and health [1-3]. This reason contributes to the development of lead-free solders that is friendly and green to the environment, where the directives on the restriction of hazardous substance (RoHS) and Waste of Electrical and Electronic Equipment (WEEE) play an important role in driving it. In the past studies and researches, it is found that the eutectic Sn-0.7Cu solder is one of the most trusted lead-free solder in replacing the lead solder [4-8].

In last decades, many researches have been done in order to study the thermal behaviour of the lead-free solder and its resulted microstructural after solidification process.

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Schindler et al. studied on the undercooling of Sn-Cu solder alloys with different Cu content from 0 to 3 wt.% and found that only little influence by Cu composition in the degree of undercooling. As different microstructural formation gives rise to a different mechanical properties of solder joint, Ventura et al. focused on the morphologies forming during the eutectic growth in binary Sn-Cu solder alloys with different growth rate of directionally solidification [9, 10]. In order to improve the solder consistency in application, Silva et al. investigated the effects of Ag and Cu minor addition into the Sn-Bi solder by directional solidification, resulted in the different microstructural formation and changing in the tensile and ductility properties [11].

In the application, solder is always related to its soldering interface since the reactions between the solder and substrate are occurred during solidification with a degree of undercooling, affecting the microstructural formation of solder joint that contributes to a different performance of the electronic devices; while most of the studies were done on copper substrate. Therefore, the purpose of this study is to investigate the influence of ENIG substrate to the Sn-0.7Cu solder by thermal behaviour and microstructural change where this Sn-0.7Cu solder will act as a control in the whole research.

2 Experimental Procedures

2.1 Sample preparation

The pure metal ingot of Sn-0.7Cu was supplied by Nihon Superior Co. Ltd., Japan. The Sn-0.7Cu solder alloy was first melted in the electric resistance furnace at 350 °C for 1 hour and then casted onto a stainless-steel mould. A several casted metal sheets were remained for the analysis and observation for solder, while the others were rolled into 50 µm thickness of foils and then punched with 3 mm diameter round shape puncher. Next, the 3 mm punched metal foils were put on the Pyrex sheet inside the reflow oven after applying the rosin mildly activated (RMA) flux on it for the purpose of 900 µm solder ball formation in a sphere shape by cause of surface tension. A several solder balls were remained for the analysis, while the others were reflowed on the substrate with ENIG surface finish after applying the RMA flux.

2.2 Thermal analysis

By using thermal analysis instruments which is differential scanning calorimeter (DSC) model Q10, 5 mg of Sn-0.7Cu metal sheet was analysed to obtain the thermal behaviour of solder. To study the thermal behaviour of Sn-0.7Cu/ENIG, 3.2 mg of solder ball with RMA flux was put on the 0.8 mg of ENIG substrate as the test sample. With the heating and cooling rate of 10 °C/min during the test, the sample was heat up to 270 °C and then cooled down to 30 °C in an inert nitrogen gas chamber to collect the endothermic and exothermic curves for analysis.

2.3 Microstructural analysis

The Sn-0.7Cu casted metal sheet and the reflowed Sn-0.7Cu/ENIG were polished and etched with the organic solderability preservative (OSP) for the microstructural observation and elemental analysis by using scanning electron microscope (SEM) model JEOL JSM 6460LA equipped with Energy Dispersive X-ray (EDX).
3 Result and Discussions

3.1 Thermal behaviour

The melting and cooling characterization of solder plays an important role in affecting the solder joint properties contributes to the electronic packaging performance. The thermal behaviour of the samples was carried out by using DSC analysis at the heating and cooling rate of 10 °C/min to mimic the application of ball-grid array (BGA) [13]. The DSC results are displayed in the Fig. 1, Table 1 and Table 2. The thermal behaviour of Sn-0.7Cu solder on the substrate with ENIG surface coating was tested besides the thermal behaviour of Sn-0.7Cu solder itself. Sn-0.7Cu and Sn0.7Cu/ENIG are heated up and the endothermic reaction is started at 228.00 and 228.26 °C respectively as the heating T onset. The heating curves are then reaching the peaks at 231.59 and 232.61 °C for Sn-0.7Cu and Sn0.7Cu/ENIG respectively as Tm. The Sn-Cu binary phase diagram is illustrated in Fig. 2. As can be viewed in the Sn-Cu equilibrium diagram, the T onset and Tm of the DSC curves are resulted from the phase changing of (Sn+ η') to liquid at the temperature of 227 °C. These DSC results are agreed by the study of Cho et al. [14], where the similar findings are reported.

On the other hand, the pasty range is formulated as:

\[
Pasty\ range = Heating\ Tendset - Heating\ Tonset
\]

where heating Tendset is the liquidus temperature and Tonset is the solidus temperature when heating [13, 15]. From Table 1, the calculation shows that the pasty range for Sn-0.7Cu and Sn-0.7Cu/ENIG is 10.27 and 11.21 °C. With the existing of substrate, the pasty range is slightly increased compared to solder itself since soldering process has taken part between the solder and substrate when heat applied. Besides the pasty range, the degree of undercooling is another main factor influencing the solder joint reliability that determines the solidification behaviour of the solder. The undercooling is defined as the difference between the beginning point of the melting (heating Tonset) in heating curve and the beginning point of solidification (cooling Tonset) in cooling curve [16]; formulated as:
Undercooling, $\Delta T = \text{Heating } T_{\text{onset}} - \text{Cooling } T_{\text{onset}}$ (2)

The undercooling degree of Sn-0.7Cu and Sn-0.7Cu/ENIG is 32.19 and 31.45 °C respectively. With the existing of substrate, the degree of undercooling is slightly decreased compared to solder itself. Cho et al. demonstrated the same trend of results that the undercooling of Sn-rich solder alloys is reduced when it reacted with various under bump metallurgies (UBMs). The wettable surface of UBMs facilitates a heterogeneous nucleation of $\beta$-Sn phase during solidification [14]. In this study, the substrate with the surface coating of ENIG has provided a wettable surface to the solder for the soldering process of elemental diffusion and dissolution from substrate and the $\beta$-Sn nucleation in solder during solidification, causing the reduction of undercooling degree.

Table 1. Heating peak ($T_m$), solidus temperature (heating $T_{\text{onset}}$), liquidus temperature (heating $T_{\text{endset}}$) and pasty range for Sn-0.7Cu and Sn-0.7Cu/ENIG.

| Sample        | $T_m$ (°C) | $T_{\text{onset}}$ (°C) | $T_{\text{endset}}$ (°C) | $T_{\text{onset}} - T_{\text{endset}}$ (°C) |
|---------------|------------|-------------------------|---------------------------|-----------------------------------|
| Sn-0.7Cu      | 231.59     | 228.00                  | 238.27                    | 10.27                             |
| Sn-0.7Cu/ENIG | 232.61     | 228.26                  | 239.46                    | 11.21                             |

Table 2. Starting point of solidification (cooling $T_{\text{onset}}$) and degree of undercooling ($\Delta T$) for Sn-0.7Cu and Sn-0.7Cu/ENIG.

| Sample        | $T_{\text{onset}}$ (°C) | $\Delta T$ (°C) |
|---------------|--------------------------|-----------------|
| Sn-0.7Cu      | 195.81                   | 32.19           |
| Sn-0.7Cu/ENIG | 196.81                   | 31.45           |

3.2 Microstructure observation

The SEM image in Fig. 3 shows that a network band is formed among the matrix in Sn-0.7Cu solder alloy. The research by Zeng et al. states that this network band is the eutectic mixture consists of Sn and a small fraction of faceted intermetallic compound Cu6Sn5 as shown in Fig. 4; while its white color area is the primary $\beta$-Sn dendrites [17]; as agreed in other studies too [18]. As a result, Sn-0.7Cu solder only contains the elements of Sn and Cu in its microstructure.

Fig. 3. SEM image of Sn-0.7Cu solder alloy.

Fig. 4. Fully solidified microstructure of Sn-0.7Cu [17].
Fig. 5. SEM results of Sn-0.7Cu soldered on ENIG substrate. (a) Sn-0.7Cu/ENIG (b) Primary (Cu,Ni)₆Sn₅ (c) Interfacial (Cu,Ni)₆Sn₅ (d) EDX on primary (Cu,Ni)₆Sn₅ (e) EDX on β-Sn (f) EDX on interfacial (Cu,Ni)₆Sn₅.

The microstructural of Sn-0.7Cu solder has changed when it is soldered on a substrate as displayed in Fig. 5, and hence EDX analysis is carried out to understand the elemental in the microstructure. In Fig. 5a, it reveals that the formation of crystals (labelled as primary and interfacial (Cu,Ni)₆Sn₅ in figure) in the solder ball and at the interfacial between the substrate and the solder. From the EDX result of the crystal (Fig. 5b) inside the solder ball in Fig. 5d, the crystal is having the elements of Sn, Cu and Ni with the atomic percentage that forming the compound of (Cu,Ni)₆Sn₅. These crystals formed inside the solder ball is termed as the primary intermetallic compound (IMC) [19]; and the Ni elements is precipitated from the diffusion and dissolution from the substrate during the interfacial reaction [14]. Thus, the crystal formed inside solder ball after soldering in Fig. 5b is the primary (Cu,Ni)₆Sn₅ IMC due to the elemental diffusion and dissolution from the substrate.

Similar to Sn-0.7Cu solder, the Sn-0.7Cu/ENIG consists of the network band among the matrix as shown in the magnified Fig. 5c; and the EDX result in Fig. 5e explains that the area without the network is the β-Sn where it is the Sn-rich area. However, it can be seen that the β-Sn dendrites and the eutectic phase are coarser than the Sn-0.7Cu solder without the substrate, where the eutectic phase forms a better continuous network. This microstructural changes correlated to the interfacial reactions during soldering is due to the reduction of undercooling degree. According to the study by Cho et al., the temperature of nucleation and growth during the solidification state was higher than the solder without
substrate due to the interfacial reactions resulted in the decreasing of the undercooling degree; and hence the solidifying grains were grow faster when this temperature raises leading to the formation of larger grain structure [14].

Furthermore, due to the interfacial reaction between the solder and substrate during soldering process, there is the growth of a crystal layer at the interfacial area of the solder and substrate as shown in Fig. 5c. Similar to the EDX result of primary IMC, Fig. 5f exhibits the interfacial crystals are formed by the Sn, Cu and Ni as the \((\text{Cu,Ni})_6\text{Sn}_5\) IMC. The elements from substrate are diffused and dissolved into the solder during the interfacial reactions when heat is applied and resulting in the formation of IMC as reported by other researchers [14, 20-22]. The addition of other elements into the solder has reduced the degree of undercooling since the nucleation of new IMC precipitates has been started during the solidification process [18]. Other researches have also revealed the similar results that the heterogeneous nucleation sites for \(\beta\)-Sn dendrites are provided by the primary IMCs causing the reduction of undercooling degree [23, 24].

4 Conclusion

The pasty range of Sn-0.7Cu/ENIG is higher than Sn-0.7Cu while its degree of undercooling is lower due to the diffusion and dissolution of elements from substrate into the solder and the \(\beta\)-Sn nucleation when solder solidifies during the interfacial reactions. Both microstructures of Sn-0.7Cu and Sn-0.7Cu/ENIG consist of primary \(\beta\)-Sn and eutectic Cu6Sn5 while Sn-0.7Cu/ENIG has another extra 2 features which are the primary \((\text{Cu,Ni})_6\text{Sn}_5\) and interfacial \((\text{Cu,Ni})_6\text{Sn}_5\) due to the elemental diffusion and dissolution from substrate. The \(\beta\)-Sn dendrites and the eutectic phase of Sn-0.7Cu/ENIG are coarser than the Sn-0.7Cu due to the reduction of undercooling degree.

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