The influence of Copper and Bismuth element in Sn-Ag solders and ENIMAG substrate

Jaidi Zolhafizi¹ and Osman. Saliza Azlina¹,*
¹Faculty of Mechanical and Manufacturing Engineering, UTHM, 86400 Batu Pahat, Johor, Malaysia

Abstract. The addition of copper and bismuth elements in Sn-Ag solders on interfacial reaction during reflow soldering and isothermal aging of SA25 and SACB25051 was investigated. The growth of intermetallic compound (IMC) was characterized by using scanning electron microscopy (SEM), optical microscope (OM) and energy dispersive x-ray (EDX). The results show the irregular circle shapes of \((\text{Cu,Ni})_6\text{Sn}_5\) IMC at the interface of solder joint for SA25 while rod-like shape for SACB25051 during both reflow soldering process and isothermal aging. The SACB25051 solder showed the thinner IMC thickness compared to SA25 solder for both conditions. The Cu and Bi element in Sn-Ag solder promotes a slower growth rate of IMC formation during interaction. The thickness and morphology of the IMC for both solders increase gradually with increasing of aging time.

1 Introduction

The expanding green technology concerns due to toxic element in Sn-Pb solders caused the development of many lead-free solders are growing rapidly in line with the Restriction of Hazardous Substances (RoHS) Regulation [1]. Recently, there are several promising candidates can replace the Sn-Pb including Sn-Ag-Cu [2,3], Sn-Ag [4,5] and Sn-Ag-Bi [2]. Even Sn-Ag-Cu (SAC) is one of the most popular lead-free solder system, it still have their own drawback where the melting-point of Sn–Ag–Cu system is higher than that of Sn–Pb solders. This can cause the soldering temperature were increased and slightly deteriorated the processing performance of the solder [2]. However, the additional of bismuth (Bi) element to tin based solders can reduce melting temperature [2,6] and improve processing performance of the solder [7].

Since several reports have shown that the doping element can improve the properties and performance [6,8], and also can reduce the growth rate of IMC layer [9]. Thus, the aim of this paper is to investigate the influence of copper and bismuth element in Sn-Ag solders and the ENIMAG substrate on intermetallic growth. The samples of isothermal aging also been investigated in order to compare with as-reflowed samples.

* Corresponding author: salizaz@uthm.edu.my
2 Materials and methods

The double type copper polymer (FR-4) was prepared as substrate materials with dimensions of 52 mm x 72 mm x 1.2 mm. The depositions of electroless nickel/immersion silver (ENImAg) were coated to the substrates. The plating baths for both substrates were maintained at 90°C for 1 hour and 40°C for 8 minutes, respectively. The Sn-2.5Ag (SA25) and Sn-2.5Ag-0.5Cu-1.0Bi (SACB25051) solder balls with a diameter of 500 μm was arranged on the substrates. The reflow process will undergo to 230°C and kept for 20 minutes. The sample then were subjected into the isothermal aging process at 150°C for 250 hours. Several characterization was carried out via cross-sectional and top surface examination to identify the type, thickness and morphology of IMC by using the scanning electron microscope (SEM) and an image analyzer.

3 Results and discussion

3.1 Top view examination

During the reflow soldering process, there are ternary compounds were detected at the interface between solder bump and Cu/ENIMAG substrate. Fig. 1 shows the images of Sn-2.5Ag (SA25) and Sn-2.5Ag-0.5Cu-1.0Bi (SACB25051) after exposed in the reflow soldering and isothermal aging process, respectively. The results show that only (Cu,Ni)6Sn5 IMC was observed at the interface for both solders during reflow soldering as well as isothermal aging. This is due to the diffusion/dissolution process between solder and substrate when the atoms moving in and out through a boundary, where Cu-Ni-Sn IMC layers might be nucleate [4]. The composition of (Cu,Ni)6Sn5 IMC was confirmed by energy dispersive x-ray (EDX) spectrum analysis as in Fig. 2. Meanwhile, a new (Ni,Cu)3Sn4 IMC layer was created at the interface during the solid state reaction. Even, there are obstacles existed at the boundary due to (Cu,Ni)6Sn5 formation, the Cu atoms are still diffuse from the substrate and solder at the slow and limited rate process. In terms of IMC morphology, the irregular circle shapes of IMC were observed at the solder joint for SA25 while rod-like shape for SACB25051 during both reflow soldering and isothermal aging process as shown in Fig. 1. The continuous heat exposure to the substrate during isothermal aging made the IMC grain size became bigger and denser. The continuous growth of IMC has been recorded until aging duration reached 250 hours. These results are consistent with previous research [10, 11].

3.2 Top view examination

Fig. 2 represents the cross-sectional examination during reflow soldering and isothermal aging for SA25 and SACB25051 solders with ENIMAG finish. After reflow soldering, the (Cu,Ni)6Sn5 layer of SACB25051 solder shows a thinner IMC than SA25 solder where the average thicknesses are 2.86 μm and 3.57 μm, respectively. Meanwhile, the total of IMC thickness for both SA25 and SACB25051 solders after exposing in isothermal aging shows a similar trend with reflow soldering where the IMC thickness recorded as 3.94 μm and 3.13 μm, respectively as illustrated in Fig. 4. From observation, the growth of IMC for both solders increase gradually with increasing the aging time. It was realized that Cu and Bi element in Sn-Ag solder managed to change the IMC thickness to be thinner than Sn-Ag solder. This explains that both Cu and Bi manage to promote a slow diffusion rate of the interaction between solder and ENIMAG, and then causes retardation of IMC growth. This statement also has a good agreement with previous researchers [12,13].
Fig. 1 SEM images of top surface morphology with magnification x4000 for SA25 and SACB25051. (a, b) reflow and (c, d) aging 250 hours.

Fig. 2. EDX spectrum of (Cu,Ni)₆Sn₅ IMC formation.
Fig. 3 Optical microscope images of cross sectional morphology with magnification x500 for SA25 and SACB25051. (a, b) reflow and (c, d) 250 hours.

| TYPE OF SOLDER | THICKNESS OF IMC (μm) |
|----------------|-----------------------|
| Reflow         | 3.57                  |
| 250 hours      | 3.94                  |
| SACB25051      | 2.86                  |
| SACB25051      | 3.13                  |

SA25: (Cu,Ni)$_6$Sn$_5$ (Ni,Cu)$_3$Sn$_4$
SACB25051: (Cu,Ni)$_6$Sn$_5$ (Ni,Cu)$_3$Sn$_4$

Fig. 4 The total thickness of IMC for SA25 and SACB25051 solders.
4 Conclusion

From the investigations, the following conclusions are successfully made:

1) As-reflow condition, the main intermetallic was formed between both types of lead-free solders with an ENIMAG surface finish are $(\text{Cu,Ni})_6\text{Sn}_5$ IMC while $(\text{Ni,Cu})_3\text{Sn}_4$ IMC was created beneath the $(\text{Cu,Ni})_6\text{Sn}_5$ after the isothermal aging process.

2) The thickness of SACB25051 solder is thinner than SA25 solder for both reflow and aging condition. The Cu and Bi element in Sn-Ag solder promotes a slower growth rate of IMC formation.

3) The thickness and morphology of the IMC for both solders increase gradually with increasing of aging time.

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