Microstructure evolution in Sn–Bi and Sn–Bi–Cu solder joints under thermal aging

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Abstract

Binary eutectic Sn–Bi and ternary Sn–Bi–Cu alloys were fabricated and soldered to conductor metallized substrates to study the interfacial morphology and microstructural evolution of the joints under thermal aging. Different types of intermetallic compound (IMC), such as Cu$_6$Sn$_5$, (Cu, Ni)$_6$Sn$_5$ and Ag$_3$Sn, are observed among various metallized substrates including Cu/FR4, Ni/Cu/FR4, Cu/Al$_2$O$_3$ and Pt–Ag/Al$_2$O$_3$. Three major effects of aging on the microstructure of the solder joints are observed. First, the coarsening rate of the Bi-rich phase in the solder joint under thermal aging at 120°C is reduced by adding 1 wt.% Cu to the 42Sn–58Bi solder. Second, the Ag$_3$Sn IMC forms planar layer at the solder/PtAg interface, while the Cu$_6$Sn$_5$ intermetallic grows as scallop-like grains into the solder at the Cu/solder interface. Third, the growth of Ag$_3$Sn intermetallic in the SnBi–1Cu/PtAg solder joint is slower than that in the 42Sn–58Bi/PtAg joint after thermal aging at 120°C.

Keywords: Solder; Intermetallic compound; Thermal aging; Interfacial morphology; Microstructure

1. Introduction

Solder joint is an essential part of electronic devices since it plays a key role not only as an electrical connection but also as a mechanical bond [1,2]. Currently, solder joints with higher reliability is demanding because the trend in electronic package is to make products smaller and faster. With appropriate joint design, the use of solder alloys with excellent properties, and the employment of a better process, reliable joints are obtained. The eutectic SnPb alloys are the most widely used solder material today [1,3–6]. However, there are environmental concerns about the toxicity of Pb in the SnPb solder alloys [3–5,7–12]. Thus, it is a research focus in recent years to develop alternative Pb-free solders. During soldering, a considerable strain is produced in the board [13]. Fortunately, the residual strain may be reduced by using a lower melting point solder. The eutectic SnBi alloy is a possible Pb-free solder for low temperature soldering due to its low melting temperature. When devices to be soldered are subject to thermal damage, low temperature soldering is necessary [3,14]. Low temperature soldering can also reduce the damage of thermal cycling caused by thermal expansion mismatch among various materials in an electronic package [14].

The tensile strength of the eutectic SnBi solder is higher than that of the eutectic SnPb solder [1,13]. In addition, the 42Sn–58Bi solder has a better creep resistance than the eutectic Sn–Pb solder [1,7,15]. However, the 42Sn–58Bi solder alloy exhibits noticeable microstructure coarsening during thermal aging [7,8,10,12,15]. The microstructure instability at elevated temperature can be suppressed by incorporating fine dispersoid particles into the eutectic SnBi solder alloys.

The solder microstructure and the growth of intermetallic compound (IMC) at the solder/metallization interface significantly influence solder joint reliability. The IMC can be a source of mechanical weakness in soldered joints due to its brittle cracking, or delimitation. With the increase of aging time, the fracture occurs at a different position from that of as-soldered joints [16,17]. Characterizing the formation and growth of IMC in the solder joint is thus critical and models were employed to demonstrate the interfacial phase transformation using an effective approach by Lee and Duh [18]. Interfacial morphology and phase analysis were also revealed in Sn–Cu solder joints [19,20]. Recently, Wei and Duh [21] reported the effect of thermal aging on Sn–Ag solder joints. Thermal cycling test in Sn–Bi and Sn–Bi–Cu solder joints was also investigated [22]. This study is aimed to evaluate the effect of the thermal aging on the microstructural evolution and IMC growth for the Sn–Bi solder on various metallized substrate. Morphology variation and phase transformation of the solder joint will be investigated. The
influence of Cu addition to the binary Sn–Bi solder is also discussed.

2. Experimental procedures

2.1. Fabrication of solder alloys

The eutectic Sn–Bi and ternary SnBi–1 wt.% Cu solder alloys were fabricated from raw materials including pure tin, bismuth and copper by vacuum melting with continuous rotation for the purpose of homogenization.

The composition of the as-fabricated binary Sn–Bi solder as measured by electron probe microanalyzer (EPMA, JXA-8800M, JEOL, Japan) is 42.4 wt.% Sn–57.6 wt.% Bi, which is fairly close to the eutectic 42Sn–58Bi in the phase diagram. As to the ternary solder, the measured composition is 43.2 wt.% Sn–55.8 wt.% Bi–1.0 wt.% Cu. There is a little deviation from the nominal 41.6 wt.% Sn–57.4 wt.% Bi–1.0 wt.% Cu possibly due to Bi loss in the melting.

Metallized ceramic substrates of Cu/Al2O3 and PtAg/Al2O3 were dipped into a batch of molten as-fabricated solders at 200°C, and followed by reflowing. Thus, the as-fabricated solder/conductor/Al2O3 joint was derived. On the other hand, a commercial eutectic 42Sn–58Bi solder paste with 88 wt.% metal and 12 wt.% RMA flux was applied to the FR4 substrate metallized with either Cu or Au/Ni/Cu. An 1206 LCCC capacitor was soldered on Cu metallized FR4, while an 8-pin SMT was soldered on the Au/Ni/Cu metallized FR4. Schematical diagrams of solder joints are shown in Fig. 1.

2.2. Thermal aging

Solder joints were aged at 100 or 120°C for various time to evaluate the morphology and IMC growth near the interface of the joints. Soldered FR4 substrates were aged at 100°C, while soldered Al2O3 substrates were aged at 120°C.
2.3. Microstructural characterization

The phase and crystal structure of the solder joints were identified with an X-ray diffractometer with a wavelength of Cu Kα (λ = 1.5406 Å). The interfacial morphology of the joints was analyzed with a scanning electron microprobe. The compositions and X-ray mapping were evaluated with an EPMA.

3. Results and discussion

3.1. Morphology of solder/conductor/FR4 assembly

Figs. 2 and 3 show the morphology and X-ray mapping of the eutectic SnBi/Cu/FR4 solder joint before and after 50 days aging at 100°C, respectively. The thickness of the Cu conductor, measured with an α-step, is about 20 μm. Only...
one IMC is observed at the interface between the 42Sn–58Bi solder and the Cu conductor. The phase identification of the intermetallics was further characterized by EPMA. As indicated in Fig. 4, the stoichiometry of the IMC at the 42Sn–58Bi/Cu interface is evaluated to be Cu₆Sn₅ after series of quantitative analysis.

Figs. 5 and 6 exhibit the morphology and X-ray mapping for the eutectic 42Sn–58Bi alloy soldered on the Au/Ni/Cu/FR4 coupons before and after 100 days aging at 100°C. In practice, gold is extensively used in printed circuit board fabrication due to its good wettability, conductivity, and corrosion resistance, while nickel is used as a diffusion barrier to suppress the growth of IMC [23]. It should be noted that the Bi-rich phase of the eutectic 42Sn–58Bi solder is coarsened during thermal aging. Originally, the thickness of the gold layer is less than 1 μm. However, the gold layer disappears after soldering due to the high solubility of Au in Sn at 200°C. Since the specimen is very small, the phase of IMC at the solder/Ni/Cu interface cannot be identified by conventional XRD. Nevertheless, the structure of IMC can be checked from the concentration profiles by EPMA as indicated in Fig. 7. Although the exact stoichiometry of
IMC cannot be observed directly from Fig. 7, a replot of the concentration sum of Cu plus Ni, instead of individual Cu and Ni, within the IMC region gives the ratio of (Cu + Ni) to Sn close to 6:5, as shown in Fig. 8. This indicates the presence of (Cu, Ni)$_6$Sn$_5$ phase in the IMC.

3.2. Morphology evaluation and phase identification of the solder/conductor/Al$_2$O$_3$ assembly

The morphology and X-ray mapping of the 42Sn–58Bi/Cu/Al$_2$O$_3$ assembly before and after 120°C aging for 16 and 36 days are shown in Figs. 9–11, respectively. The phase identification was further verified by EPMA. As described in the previous section, the Cu$_6$Sn$_5$ IMC is formed at the solder/Cu interface, and the Bi-rich phase of the eutectic SnBi solder is coarsened after thermal aging.

In order to evaluate the effect of alloy addition on the microstructure coarsening, the ternary SnBi–1Cu solder is tested under the same condition. The corresponding micrographs of the SnBi–1Cu/Cu/Al$_2$O$_3$ joint are indicated in Figs. 12–14. The intermetallics formed at the SnBi–1Cu/Cu interface is also identified to be Cu$_6$Sn$_5$. 

Fig. 6. Micrographs of 42Sn–58Bi/Ni/Cu/FR4 solder joint after 100 days aging at 100°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.
However, there is no significant coarsening for the Bi-rich phase in the SnBi–1Cu solder during thermal aging as shown in Figs. 12–14. To quantify the coarsening rate of Bi-rich phase, mean intercept length of the Bi-rich phase is measured. Mean intercept length ($L$) is a quantitative length parameter which provides an unique, assumption-free value for any space-filling structure, regardless of grain shape, size, or position [24]. The general expression of mean intercept length, $L$, for space-filling grains is

$$L = \frac{L_L}{N_L}$$

where $L_L$ is the sum of linear intercept lengths divided by total test line length, and $N_L$ is the number of point features.

Fig. 7. Electron microprobe trace across the intermetallic layer of the eutectic SnBi/Cu/FR4 assembly after aging at 100°C for 100 days (raw data).

Fig. 8. Electron microprobe trace across the intermetallic layer of the eutectic SnBi/Cu/FR4 assembly after aging at 100°C for 100 days (sum of Cu and Ni concentration is indicated).
Fig. 9. Micrographs of the eutectic SnBi/Cu/Al2O3 joint before aging: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.

Fig. 10. Micrographs of the eutectic SnBi/Cu/Al2O3 joint after 16 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.
Fig. 11. Micrographs of the eutectic SnBi/Cu/Al₂O₃ joint after 36 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.

Fig. 12. Micrographs of the SnBi–1Cu/Cu/Al₂O₃ joint before aging: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.
Fig. 13. Micrographs of the SnBi–1Cu/Cu/Al₂O₃ joint after 16 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.

Fig. 14. Micrographs of the SnBi–1Cu/Cu/Al₂O₃ joint after 36 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Cu mapping.
Table 1
Mean intercept length (μm) of the Bi-rich phases at various aging time

<table>
<thead>
<tr>
<th>Aging time (days)</th>
<th>0</th>
<th>4</th>
<th>9</th>
<th>16</th>
<th>25</th>
<th>36</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnBi/Cu</td>
<td>1.01</td>
<td>1.03</td>
<td>1.48</td>
<td>2.50</td>
<td>2.81</td>
<td>4.80</td>
</tr>
<tr>
<td>SnBi–1Cu/Cu</td>
<td>1.01</td>
<td>1.05</td>
<td>1.06</td>
<td>1.06</td>
<td>1.05</td>
<td>1.09</td>
</tr>
<tr>
<td>SnBi/PtAg</td>
<td>1.04</td>
<td>1.08</td>
<td>1.53</td>
<td>2.08</td>
<td>3.02</td>
<td>4.69</td>
</tr>
<tr>
<td>SnBi–1Cu/PtAg</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.13</td>
<td>1.22</td>
<td>1.20</td>
</tr>
</tbody>
</table>

\[ N_L = \frac{P}{L_T} M \]  \hspace{1cm} (2)

where \( P \) is the number of point elements or test points, \( L_T \) is the total test-line length, and \( M \) indicates magnification.

The mean intercept length of the Bi-rich phase in the 42Sn–58Bi/Cu/Al2O3, SnBi–1Cu/Cu/Al2O3, 42Sn–58Bi/PtAg/Al2O3, and SnBi–1Cu/PtAg/Al2O3 joints after various aging time at 120°C is listed in Table 1. Meanwhile, the mean intercept length of the Bi-rich phase vs. aging time for the solder/Cu and the solder/PtAg assemblies is indicated in Figs. 15 and 16, respectively. In the case of Cu metallized assembly, the mean intercept length of the Bi-rich phase for the SnBi/Cu joint is increased over four times after aged for 36 days, while it remains essentially the same for the SnBi–1Cu/Cu joint, as shown in Fig. 15. Similar trend is revealed in the Pt–Ag metallized assembly. Fig. 16 shows that the mean intercept length of the Bi-rich phase for the SnBi/Pt–Ag joints is increased nearly five times after aged for 36 days, while the increase is only around 10% for the SnBi–1Cu/Pt–Ag joint. It is obvious that the coarsening rate of the Bi-rich phase during thermal aging is greatly reduced by adding trace amount of copper into the eutectic SnBi solder alloy. Examination of the Cu–Bi and Cu–Sn phase diagrams indicates that Cu is insoluble in Bi and has limited solubility in Sn (0.01 at.% Cu at 231°C). Thus, copper is present in the solder as small Cu6Sn5 intermetallic particles which may pin the interface boundaries and thus reduces the coarsening of Bi-rich phases.

Figs. 17–22 exhibit the microstructure and X-ray mapping of the 42Sn–58Bi/PtAg/Al2O3 and the SnBi–1Cu/PtAg/Al2O3 joints after 120°C aging for 0, 16, and 36 days. The electron probe microanalysis (EPMA) for the eutectic SnBi and the SnBi–1Cu solder on the PtAg/Al2O3 assembly is illustrated in Figs. 23 and 24, respectively. Only one IMC is found at the solder/PtAg interface. The stoichiometry of the intermetallic layer is characterized to be Ag3Sn.

According to the micrographs of X-ray mapping for the solder/Cu/Al2O3 assembly shown in Figs. 9–14, the growth of Cu6Sn5 intermetallics requires the interdiffusion of Sn.
and Cu. It is argued that the growth of the Cu₆Sn₅ intermetallics is a thermally activated process which depends on both the Sn and Cu diffusion. From theoretical point of view, the element with lower melting temperature has larger diffusion coefficient in the binary diffusion couple. However, diffusion of interstitial atoms is much more easier than that of substitutional atoms. In addition, extensive interstitial solid solutions occur only if the solute atom has an apparent diameter smaller than 0.59 that of the solvent [25]. Since Sn has a lower melting point but a much larger atomic volume (32.1 × 10⁻²² cm³ per atom) than Cu does (7.5 × 10⁻²² cm³ per atom), the diffusion coefficient of Cu may be comparable to that of Sn in the Sn–Cu couple. The corresponding micrographs for the solder/PtAg/Al₂O₃ joint indicate that the growth of the Ag₃Sn intermetallics is dominated by the Sn diffusion. It is argued that this is attributed to the fact that the melting point of Sn is lower than that of Ag, and Ag would not diffuse interstitially into Sn since the atomic volume of Ag (18.4 × 10⁻²² cm³ per atom) is not small. Therefore, Sn may diffuse faster in the Sn–Ag couple.

In general, there are two limiting conditions for intermetallic growth in the alloy system. One is diffusion control mechanism and the other is interface control mechanism. Fig. 25 plots the intermetallic (Ag₃Sn) thickness vs. the square root of aging time for the eutectic SnBi/PtAg/Al₂O₃ and the SnBi–1Cu/PtAg/Al₂O₃ joints at 120°C. The regression analysis indicates that the data are best fitted with a parabolic time dependence. This implies that the growth of the Ag₃Sn intermetallics is diffusion controlled. Moreover, it should be pointed out that the thickness of Ag₃Sn is reduced in the SnBi–1Cu/PtAg solder joint as compared to the eutectic SnBi/PtAg joint. A similar phenomenon was discovered by Wu et al. [27], who reported that the growth of intermetallics is strongly affected by the trace element added to the solder. The addition of Cu enhances the activation energy of Cu₆Sn₅ formation, and thus suppresses the growth of Cu₆Sn₅ IMC [26,27]. In addition, it is apparent that the growth rate of Ag₃Sn intermetallics is higher than that of the Cu₆Sn₅ intermetallics, as shown in Figs. 9–11 and 17–19. A recent study by Wei and Duh [21] revealed that the diffusion coefficient for Ag₃Sn in the SnAg/PtAg joint is 23.38 × 10⁻¹³ cm² s⁻¹ at 120°C, while that for Cu₆Sn₅ in the SnAg/Cu joint is 6.76 × 10⁻¹³ cm² s⁻¹ at 200°C. It is argued that the faster growth rate of Ag₃Sn intermetallics is attributed to the lower melting point of Ag than that of Cu.
Fig. 17. Micrographs of the eutectic SnBi/PtAg/Al₂O₃ joint before aging: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Ag mapping.

Fig. 18. Micrographs of the eutectic SnBi/PtAg/Al₂O₃ joint after 16 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Ag mapping.
Fig. 19. Micrographs of the eutectic SnBi/PtAg/Al₂O₃ joint after 36 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Ag mapping.

Fig. 20. Micrographs of the SnBi–1Cu/PtAg/Al₂O₃ joint before aging: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Ag mapping.
Fig. 21. Micrographs of the SnBi–1Cu/PtAg/Al₂O₃ joint after 16 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Ag mapping.

Fig. 22. Micrographs of the SnBi–1Cu/PtAg/Al₂O₃ joint after 36 days aging at 120°C: (a) SEI; (b) Sn mapping; (c) Bi mapping; (d) Ag mapping.
Unlike Ag₃Sn, the Cu₆Sn₅ IMC does not form a layer at the interface between the solder and the Cu conductor, instead it grows as scallop-like grains into the solder. Comparison between Figs. 14 and 22, including SEI morphology, Sn, Ag and Cu mapping, can reveal this discrepancy. Fig. 14(a) shows that the interfacial morphology for the SnBi–1Cu/Cu/Al₂O₃ is rather irregular while that of SnBi–1Cu/PtAg/Al₂O₃ is more or less planar, as indicated in Fig. 22(a). The variation in the formation of Cu₆Sn₅ and Ag₃Sn IMC in Cu metallized and PtAg metallized Al₂O₃ substrate can be schematically represented in Fig. 26. A similar phenomenon was reported by Tu and co-workers [28–32], who pointed out that the scallop-like Cu₆Sn₅ intermetallics were formed at the eutectic SnPb solder/Cu conductor in the molten state. The irregular growth of the Cu₆Sn₅ compounds is caused by dissolution of Cu into the molten solder and the coarsening of the scallop-type Cu₆Sn₅ intermetallics by Ostwald ripening.

Fig. 23. Electron microprobe trace across the intermetallic layer of the 42Sn–58Bi/PtAg/Al₂O₃ assembly after aging at 120°C for 36 days.

Fig. 24. Electron microprobe trace across the intermetallic layer of the SnBi–1Cu/PtAg/Al₂O₃ assembly after aging at 120°C for 36 days.
4. Conclusions

1. A single IMC \( \text{Cu}_6\text{Sn}_5 \) is observed in the eutectic SnBi/Cu/FR4 joint after aging at 100°C for 49 days, while \((\text{Cu}, \text{Ni})_6\text{Sn}_5\) IMC is present in the SnBi/Ni/Cu/FR4 joint after aging at 100°C for 100 days.

2. Significant coarsening of the Bi-rich phase is observed in the binary eutectic SnBi joint. However, the microstructure coarsening is substantially reduced by an addition of 1 wt.% Cu into the binary Sn–Bi solder. Identical trend is exhibited in the solder joined with both Cu and Pt–Ag metallized Al\(_2\)O\(_3\) substrate.

3. In both SnBi/Cu/Al\(_2\)O\(_3\) and SnBi–1Cu/Cu/Al\(_2\)O\(_3\) joints, \( \text{Cu}_6\text{Sn}_5 \) IMC is formed after aging at 120°C. However, \( \text{Ag}_3\text{Sn} \) IMC is observed in both SnBi/Pt–Ag/Al\(_2\)O\(_3\) and SnBi–1Cu/Pt–Ag/Al\(_2\)O\(_3\) joints.

4. The formation of \( \text{Ag}_3\text{Sn} \) IMC in the Sn–Bi–1Cu solder with PtAg metallized Al\(_2\)O\(_3\) is planar, while that of \( \text{Cu}_6\text{Sn}_5 \) intermetallic is the SnBi–1Cu solder with Cu metallized Al\(_2\)O\(_3\) is scallop-like.

5. The growth if \( \text{Ag}_3\text{Sn} \) intermetallics is diffusion controlled. The thickness of \( \text{Ag}_3\text{Sn} \) is reduced in the ternary SnBi–1Cu/PtAg joint as compared to that in the eutectic SnBi/PtAg joint.

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References
