Structural Changes of the IMC in Lead Free Solder Joints

Erika Hodúlová*, Beáta Šimeková and Ingrid Kovaříková

Faculty of Materials Science and Technology in Trnava, Institute of Production Technologies, Slovak University of Technology in Bratislava, J. Bottu 23, 917 24 Trnava, Slovak Republic

The development of Cu–Sn intermetallic compound (IMC) at the solder/Cu joints interface had been studied using five Pb-free solders as SnAg3.0Cu0.5, SnAg3.5Cu0.7, SnAg1.0Cu0.5Bi1.0, SnAg1.5Cu0.7In0.5 and SnCu0.67In2.0 alloys (composition given in mass%). The effects of Bi and In additions on the intermetallic phase formation in the lead-free solder joints with copper substrate were studied. The soldering of the copper plate was conducted at 250°C for 5 s. The solder joint reliability of SnAg3.0Cu0.5 and SnCu0.67In2.0 alloys was assessed with the thermal cycling test in the range from −40°C to 130°C. Altogether 1500 cycles were carried out. The solder joints with SnAg3.5Cu0.7, SnAg1.0Cu0.5Bi1.0 and SnAg1.5Cu0.7In0.5 alloys were subsequently aged at temperatures of 130–170°C for 2–16 days in a convection oven.

1. Introduction

Reliability in performance of electronic equipment, in the face of demands for continuing miniaturisation and the anticipated abolition of lead-containing solders, represents a major engineering challenge. Two specific challenges are facing the electronics community. The first is technical and relates to the continuous miniaturisation of equipment, which has placed increasing demands upon structural integrity and reliability of performance in service. The second challenge is environmental and arises from the demand for toxic lead to be removed from solder alloys used for interconnection. This has engendered a search for new alloys, which in turn has placed increased pressures on processing. From a reliability perspective, the most important characteristics of these solders are their tendency to form thick intermetallic layers with termination metals.1,2) During soldering, some of the metal substrate is dissolved into the molten solder. As a result, the solder becomes supersaturated with the dissolved metal and a layer of an intermetallic compound is formed at the metal–solder interface. The intermetallic layer continues to grow after solidification due to thermally activated solid state diffusion mechanisms. The formation and growth of intermetallic at the solder/substrate interface affect the solderability and reliability of electronic solder joints. Intermetallic compounds are generally much harder and more brittle than solders and can, therefore, cause brittle fractures at the interface between the solder and the metal substrate.3,4)

2. Microstructural Evaluation of Soldered Joints

The soldering of the copper plate was conducted at 250°C for 5 s. The solder joints with SnAg3.5Cu0.7, SnAg1.0Cu0.5Bi1.0 and SnAg1.5Cu0.7In0.5 alloys were subsequently aged at temperatures of 130–170°C for 2–16 days in a convection oven.

2.1 Cu–SnAgCu

The thickness of IMC (Fig. 1) increases with the increasing temperature and ageing time. At the temperature of 150°C and ageing time of 16 days, the Cu6Sn compound reaches a thickness of 4.72 µm, while the thickness of Cu6Sn5 compound reaches 11.41 µm. At the temperature of 170°C and ageing time of 16 days, the Cu6Sn5 compound thickness is much thicker, achieving 45.38 µm. At this temperature, we cannot speak of a continuous layer of the given compound; the structure is peaked.

When compared with the SnAg solder, the Cu6Sn5 compound of SnAgCu solder grew to greater thickness (Table 1 and 2).

2.2 Cu–SnAgCuBi

During the subsequent solid state ageing (Fig. 2), the layer continued to grow. The Cu6Sn5 layer is formed by nucleation during soldering between the solid copper substrate and liquid Sn-based lead free solder. At early stages, the layer is expected to grow in the horizontal direction until the grains start impinging one another. The scallop-like shape of this phase is probably a result of the grain coarsening. The scallop-like shape disappears at later stages of ageing which suggests a change in the growth mechanism to the steady growth in the perpendicular direction to the interface.

2.3 Cu–SnAgCuIn

When being aged for a longer time, the Cu6(Sn,In)5 compound grows markedly (see Fig. 3). At the temperatures of 150°C and 170°C, the Cu6(Sn,In)5 compound forms an uneven structure. At the ageing temperature of 170°C and ageing time 384 h, thickness of the Cu6(Sn,In)5 layer is 62 µm, which induced poor mechanical properties of the joint, leading to degradation. This ageing temperature of solder is too high; it is therefore recommended to choose a lower one.

In the second stage the solder joint reliability of SnAg3.0Cu0.5, SnAg1.0Cu0.5Bi1.0 and SnCu0.67In2.0 alloys was assessed with the thermal cycling test in the
range from \(-40^\circ\text{C}\) to \(150^\circ\text{C}\). Altogether 1500 cycles were carried out. The parameters of the thermal cycling test have been defined according to requirements of a major producer of electronic goods in Slovakia.

### 2.4 Cu–SnAg3.0Cu0.5–Cu

At the interface of Sn grains the creation and spreading of cracks has been observed. After the 423 cycles micro-cracks were seen in the SnAg3.0Cu0.5 solder joints. These cracks occurred in the volume of the Sn grains as well as near the interface to the Cu substrate (Fig. 4). The micro-cracks were observed also in the IMC itself. In the Cu3Sn layer Kirkendall voids have been observed.\(^8\)

### 2.5 Cu–SnAg1.0Cu0.5Bi1.0–Cu

High crystallographic disorientation of Sn grains was observed at the interface of Cu-SnAg1.0Cu0.5Bi1.0-Cu after 1500 thermal cycles. After 793 cycles first micro-cracks

---

**Table 1** Measured values of IMC thickness for SnAg solder.

<table>
<thead>
<tr>
<th>Time of ageing (day/hour)</th>
<th>Thickness of IMC SnAg ((\mu\text{m}))</th>
<th>(T = 130^\circ\text{C})</th>
<th>(T = 150^\circ\text{C})</th>
<th>(T = 170^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu/\text{Sn}</td>
<td>Cu/\text{Sn}_5</td>
<td>Cu/\text{Sn}</td>
<td>Cu/\text{Sn}_5</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1.54</td>
<td>0</td>
<td>1.54</td>
</tr>
<tr>
<td>2/48</td>
<td>1.10</td>
<td>1.62</td>
<td>1.17</td>
<td>2.12</td>
</tr>
<tr>
<td>4/96</td>
<td>2.26</td>
<td>3.43</td>
<td>2.34</td>
<td>3.83</td>
</tr>
<tr>
<td>8/192</td>
<td>2.69</td>
<td>3.60</td>
<td>3.34</td>
<td>5.14</td>
</tr>
<tr>
<td>12/228</td>
<td>3.02</td>
<td>6.29</td>
<td>5.47</td>
<td>6.90</td>
</tr>
<tr>
<td>16/384</td>
<td>4.29</td>
<td>8.01</td>
<td>6.48</td>
<td>9.32</td>
</tr>
</tbody>
</table>

---

**Table 2** Measured values of IMC thickness for SnAgCu solder.

<table>
<thead>
<tr>
<th>Time of ageing (day/hour)</th>
<th>Thickness of IMC SnAgCu ((\mu\text{m}))</th>
<th>(T = 130^\circ\text{C})</th>
<th>(T = 150^\circ\text{C})</th>
<th>(T = 170^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu/\text{Sn}</td>
<td>Cu/\text{Sn}_5</td>
<td>Cu/\text{Sn}</td>
<td>Cu/\text{Sn}_5</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1.88</td>
<td>0</td>
<td>1.88</td>
</tr>
<tr>
<td>2/48</td>
<td>0.64</td>
<td>2.65</td>
<td>0.95</td>
<td>5.17</td>
</tr>
<tr>
<td>4/96</td>
<td>0.87</td>
<td>4.12</td>
<td>1.31</td>
<td>6.19</td>
</tr>
<tr>
<td>8/192</td>
<td>1.06</td>
<td>5.52</td>
<td>2.77</td>
<td>7.84</td>
</tr>
<tr>
<td>12/228</td>
<td>2.47</td>
<td>6.33</td>
<td>4.03</td>
<td>9.25</td>
</tr>
<tr>
<td>16/384</td>
<td>3.34</td>
<td>7.04</td>
<td>4.72</td>
<td>11.41</td>
</tr>
</tbody>
</table>

---

*Fig. 1* Microstructure of the Cu-SnAg3.5Cu0.7 solder joint after ageing at \(T = 130^\circ\text{C}, 150, 170^\circ\text{C}, t = 48\) h and 384 h.\(^5,6\)

*Fig. 2* Microstructure of Cu-SnAgCuBi1.0 after ageing.\(^5,7\)

---

*E. Hodúlová, B. Šimeková and I. Kovaříková*
along the grain boundaries have been observed (Fig. 5). With the increasing number of temperature cycles a growth of the IMC layer at the interface and in the phases of the Sn matrix has been recorded. It should be noted that these cracks did not occur along the interface. An adverse effect is cracking along the interface intermetallic layer, which may initiate the brittle fracture in later stages of thermos-mechanical fatigue.8)

2.6 Cu–SnCu0.67In2.0–Cu

In the volume of solders are Cu₆(Sn, In)₅ phases of various shapes and sizes. A dominant growth of Cu₃Sn layer during cycling significantly contributes to the overall thickness of the IMC layer at the interface.9)

In the SEM micrograph of Fig. 6 the isolated micro-cracks in the IMC layer at the solder joint interface can be seen. Also some cavities and pores, which are sources for the formation and the growth of cracks can be seen. In the joints exposed to 1500 thermal cycles, cracks along the Sn-grain boundaries were observed.
3. Conclusion

PCB failure mechanisms fall into three groups: thermally induced failures, of which plated through-holes are the most important example; mechanical failures; and chemical failure mechanisms, of which dendrite growth is the most important example. Thermal fatigue in solder joints occurs because of the thermal expansion mismatch between the PCB and the component interconnected by the solder joint. During soldering, some of the metal substrate is dissolved into the molten solder. As a result, the solder becomes supersaturated with the dissolved metal and a layer of an intermetallic compound is formed at the metal–solder interface. The intermetallic layer continues to grow after solidification due to thermally activated solid state diffusion mechanisms. The formation and growth of intermetallic at the solder/substrate interface affect the solderability and reliability of electronic solder joints. Intermetallic compounds are generally much harder and more brittle than solders and can, therefore, cause brittle fractures at the interface between the solder and the metal substrate. Due to the high concentration of tin in most Pb-free solders CuSn intermetallic compounds form at the interface to the copper substrate. The Cu₆Sn₅ layer is formed during soldering and Cu₃Sn forms during solid state ageing between Cu₆Sn₅ and the Cu substrate. The layer growth is diffusion-limited and sensitive to the copper concentration in the solder. Higher copper concentration is shown to produce thicker Cu₃Sn layers. The Cu₃Sn layer formation is limited by Sn diffusion. Generally, elements diffuse through grain boundaries more rapidly than through the grain interior. A sufficient flux of Sn is needed to maintain the Cu₃Sn growth. Indium has a comparable atomic diameter to tin, it might have a greater tendency to substitute tin in intermetallic compounds than Bi, especially at high concentrations. Therefore, the retardation effect could be more pronounced for indium-containing solder compounds comparing to bismuth-doped samples. Nevertheless, the Bi effect is also significant. It has already been shown that 1% Bi may lead to an approximately 10% decrease in the growth rate constant.

The reduction of the intermetallic rate growth decreases the rate of joint degradation and increases the durability.

Acknowledgments
This research is supported by VEGA Grant No. 1/0455/14 and Grant No. APVV-0023/12.

REFERENCES