The Effects of Adding Silver and Indium to Lead-Free Solders

Even small additions of silver and indium produced improvements in the wettability, microstructure, and microhardness of lead-free solder

BY I. G. BUDI DHARMA, M. HAMDI, AND T. ARIGA

In-lead (Sn-Pb) solder alloys have been used for many years in the assembly of electronic devices. This alloy has many desirable characteristics, including low cost, low melting temperature, good manufacturability, and excellent wetting on copper (Cu) substrates and its alloys. However, the toxicity of Pb to human health and the environment has stimulated substantial research to discover a Pb-free solder suitable for electronic assemblies. Many Pb-free solder alloys have been proposed as a replacement for Sn-Pb solder, but few meet the required material properties, solderability, and cost criteria.

Pb-Free Material Selection

A number of elements can be considered to replace Pb in solder. Table 1 provides a comparison of the elements most likely to be used as the Pb replacement. Note that any substitute for Pb will increase solder cost, because Pb is a relatively inexpensive metal. Tin remains the best choice for the base metal because its melting point is lower than Cu and Ni, and it’s priced lower than gold (Au), silver (Ag), and indium (In), which are too expensive to use in the quantities required as a solder base. If either In or Ag is added, its content must small to keep the cost down. Zinc (Zn) used as a base alloy or an addition has been reported to have several drawbacks, especially its poor corrosion resistance (Ref. 1).

Clearly, the toxic metallic elements such as cadmium, thallium, and mercury can be eliminated immediately as solder element candidates (Ref. 2). Japan and Scandinavia also regard antimony as a toxic element (Ref. 3).

Improving Sn-Cu Eutectic Solder

The Sn-Cu binary alloy, which has a eutectic composition of Sn-0.7 wt-%Cu, has been considered for use in wave soldering applications because it is the least expensive of the lead-free alloy candidates (Ref. 4). Solder cost is a key consideration in wave soldering because of the need to periodically replace the entire solder bath to control contamination buildup. However, Sn-Cu eutectic solder also has poor mechanical properties compared with Sn-Ag and Sn-Ag-Cu eutectic solders (Refs. 3, 5).

In this study, small additions of Ag (0.1, 0.3, 0.5 wt-%) and 1.0 wt-% of In were added to Sn-0.7Cu eutectic alloy to improve the alloy’s wettability and mechanical properties.

Experiment Details

The solder alloys were provided by Nihon Almit Co. Ltd. Japan in bar form. The solder alloys used for this study were Sn-0.7Cu-1.0In-xAg (where x = 0, 0.1, 0.3, and 0.5). Thermal analysis of the solder alloys was performed using a DSC-50 Shimadzu differential scanning calorimeter (DSC). Small specimens, about 20 mg, were used for the DSC analysis. The heating rate was 5°C/min from room temperature to 350°C in 50 mL/min argon gas flow.

The wetting balance test was conducted using a SAT5100 Rhesca. The parameters used for wetting balance test were 5 mm/s of dipping speed with a dipping depth of 10 mm. The dipping time was 20 s, and the testing temperature was 250°C. Oxygen-free, high-conductivity (OFHC) copper sheet, 10 × 30 × 0.3 mm, was used as the substrate metal. The flux used in the experiments was RC-15SH, a commercial rosin mildly activated (RMA) from Nihon Almit Co. Ltd., Japan.

The Vickers hardness number (HV) of the solder alloy was determined by conducting a microhardness test. The parameters were 0.025 g-f of loading weight and 20 s loading time.

Table 1 — Melting Temperatures of Metals Used in Electronic Assemblies

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth (Bi)</td>
<td>271</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>1083</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>1083</td>
</tr>
<tr>
<td>Indium (In)</td>
<td>157</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>327</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>1453</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>960</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>232</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>419</td>
</tr>
</tbody>
</table>

Table 1: Melting Temperatures of Metals Used in Electronic Assemblies.

I. G. B. BUDI DHARMA (budi_de@yahoo.com) and M. HAMDI are with the Department of Engineering Design and Manufacture, University of Malaya, Malaysia; and T. ARIGA is with the Department of Material Science, School of Engineering, Tokai University, Japan.

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**Results of the Investigation**

**DSC Analysis**

The curve obtained from DSC analysis is shown in Fig. 1. Figure 1A shows the onset temperature of Sn-0.7Cu is 227.4°C. The onset temperature of the DSC heating curve is the temperature at which the solder starts to melt, or it can be marked as a solidus temperature of the solders or the eutectic temperature of a eutectic solder alloy. The addition of 1.0 wt-% In into the Sn-Cu eutectic solder lowered the onset temperature from 227.4°C to 224.4°C — Fig. 1B.

The onset and peak temperatures can be further lowered by small additions of Ag to the Sn-0.7Cu-1.0In-xAg solders. Figure 2 shows the onset and peak temperatures in the DSC curve as a function of Ag additions. The addition of 0.1 wt-% Ag slightly lowered the onset temperature from 224.4°C to 223.8°C. The addition of 0.3 wt-% Ag lowered the onset temperature to 222.1°C, and adding 0.5 wt-% Ag lowered it to 219.7°C. The peak temperatures also decreased with increasing Ag content. The DSC analysis showed that small amounts of Ag and In can effectively lower the onset and peak temperatures.

**Wetting Balance Test**

Figure 3 shows a typical wetting curve. In this force-time curve, the two most common values are used as the wettability parameters: the wetting time ($t_1$) and the maximum wetting force ($F_{\text{max}}$) (Refs. 9, 10). The times at which the solder contact angle to the specimen is 90 deg, or for the measured wetting force to return to zero are widely used as the wetting time (Ref. 11). The $F_{\text{max}}$ is obtained when the meniscus is stabilized after immersion and the measured force remains constant.

The $t_1$ and $F_{\text{max}}$ of Sn-0.7Cu-1.0In-xAg ($x = 0, 0.1, 0.3,$ and $0.5$) solders obtained from wetting balance test are displayed in Figs. 4 and 5, respectively. In Fig. 4, the addition of 0.1 wt-% Ag slightly increased $t_1$ from 2.3 to 2.5 s. However, with the addition of 0.3 wt-% Ag, $t_1$ decreased to 2.2 s and
further decreased to 2 s with the addition 0.5 wt-% Ag. As shown in Fig. 5, the addition of 0.1 wt-% Ag reduced the $F_{\text{max}}$ of the solder from 4.2 to 3.2 mN. The $F_{\text{max}}$ started to increase with the addition of 0.3 and 0.5 wt-% of Ag, which increased to 4.6 and 4.9 mN, respectively. This proved that the addition of small amounts of Ag can improve the solder’s wettability.

**Microhardness**

The microhardness of the solders with varying Ag content is displayed in Fig. 6. Additional Ag content up to 0.5 wt-% slightly reduced the Vickers hardness ($H_v$) of solders from 16.5 to 14.6 $H_v$. The result indicates that increasing the Ag content can improve ductility of the solders. Ductility of the solder is very important to insure the reliability of the joint structure. It has been reported that small additions of Ag improve the elongation by about 50% (Ref. 12).

**EPMA Result**

Figure 7 shows the electron probe microanalysis (EPMA) results of solder alloys with various Ag contents in the Sn-0.7Cu-1.0In-xAg solders. The results indicate that with increasing Ag content, the bright Sn-rich grain size becomes finer surrounded by Cu-Sn and Ag-Sn intermetallic compounds. It has been reported that the bright grains correspond to primary β-Sn phase and it is surrounded by Cu$_3$Sn$_2$ and Ag$_3$Sn intermetallic compound phases (Refs. 12, 13). Indium was observed distributed in primary grain because of its similar atomic size.

**Conclusions**

Improving the Sn-Cu eutectic solder with small amounts of Ag and In displayed promising results as a lead-free solder candidate. The onset temperature in DSC curve of Sn-Cu eutectic solder was lowered by the addition 1.0 wt-% In. Further lowering of the onset and peak temperatures was obtained by the addition of Ag. Small additions of Ag affect the wettability of solders. Higher Ag contents produced better wettability by lowering wetting time ($t_1$) and increasing maximum...
wetting force ($F_{\text{max}}$). Increasing the Ag content from 0.1 to 0.5 wt-% in Sn-0.7Cu-1.0In-xAg solders, slightly decreases its hardness. The addition of Ag makes the primary grain size of $\beta$-Sn become smaller. Based on the EPMA results, Cu-Sn and Ag-Sn intermetallic phases were observed and In atoms were distributed on the $\beta$-Sn matrix.

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References


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