Properties of Solder Joints Using Sn-Ag-Bi-In Solder

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The lead-free soldering technology has been developed all over the world while IEEE ReHS prohibits the use of lead contained solder in 2006. Sn-Ag-Cu solder of which melting point is 219°C has the highest solder joints reliability of leadfree solder materials. This melting point is much higher than that of the conventional solder of 183°C. So reflow process for low heat-resistant components on Print Circuit Board needs lower melting point solder. Sn-Zn-Bi solder with low melting point of 197°C has a high barriera to apply to electric products due to lower reliability at high temperature, in high humidity and after reheating a joint comparing to conventional solder. Adding both bismuth and indium into Sn-Ag solder alloy is effective especially for decrease of melting point of Sn-Ag solder and Sn-Ag-Bi-In solder which had a melting point of 206°C was developed. In this paper, we mentioned design of the solder alloy and soldering properties of Sn-Ag-Bi-In to the point of appearance and microstructure of solder joints concerning about the influences of temperature, humidity and heat story of joint surface after 1000 cycles at −40°C/125°C and after 1000 hours of 85°C/85%RH. But the solder joint strength of Sn-Ag-Bi-In in comparable to that of Sn-Pb eutectic solder in each test. And no significant deterioration of Sn-Ag-Bi-In solder had the same reliability as conventional solder and could be useful to expand the practical use of lead-free solder for a lot kinds of products.

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1. Introduction

Lead-containing solder joining processes have contributed substantially to the advancement of electronic products for many years. Due to the risk of lead being leached from discarded electronic circuit boards by acid rain, however, soldering technology is now in a transitional phase to lead-free soldering.1,2) The WEEE/RoHS Directives of the EU ban the use of lead in electrical products from July 2006.

The application of lead-free solder to electronic products requires a complete review of all elements involved in electronic circuit manufacturing, ranging from printed circuit boards (PCBs) and electronic components through to the manufacturing process and equipment development. In addition, ease of assembly, reliability assessment methods, and the setting of evaluation criteria setting need to be completely reexamined. Because of the enormous difficulty and cost that would be incurred by simultaneously developing material processes, equipment, components and PCBs, the selected strategy has been to use the current reflow soldering process, equipment and manufacturing process. This requires the following conditions to be applied in the development process.

(1) Solder joint quality needs to be equal to or better than that of conventional solder joints
(2) The operational process must be similar to that for lead solder (particularly reflow temperature)
(3) Current production equipment can be used.

A standard Sn-3Ag-0.5Cu solder has been selected for the solder material used in the reflow process due to its excellent joint properties. However, extending its application to all company products would require the upgrading of many components’ heat resistance to withstand the higher melting point of Sn-3Ag-0.5Cu solder, not to mention the replacement of reflow soldering equipment. The current paper describes the new challenge of searching for lower melting-point solder materials. As potential candidates to substitute for Sn-3Ag-0.5Cu solder, we studied low melting-point Sn-Ag solder materials, in particular Sn-Ag-Bi-In solder and Sn-Zn-Bi solder materials.

2. Experimental Procedure

The solders used in this study were Sn-3.5Ag-0.5Bi-3In, Sn-3Ag-2.5Bi-2.5In, Sn-3.5Ag-0.5Bi-8In, and Sn-8Zn-3Bi, with Sn-37Pb used as the reference solder(all compositions are expressed in mass %). Each solder paste was mixed with a mildly activated rosin (RMA) flux. 20 mm x 20 mm 120-pin QFPs (quad flat packages) with Sn-Bi(10μm), Au(0.01μm)/Pd (0.08μm)/Ni(0.3 μm) (from surface to inside) and Sn-Pb(10μm) plated Cu leads were reflow-soldered in air onto Cu pads of PCBs using the solder paste composed of each solder alloy. The reflow profile consisted of pre-heating at 160°C for 90 s followed by holding at above 220°C for 20 s at a peak temperature of 230°C.

The solder joint properties of the specimens were examined after 1000 heat cycles at −40°C/110°C, −40°C/125°C and −40°C/150°C in a thermal cycle test, 1000-hour humidity exposure at 85°C/85%RH in a high temperature/high humidity tests and by adding heat exposure to the solder joints on the reflow side by reflow/wave double side soldering. The solder joints’ strength was then measured using a pull test at a tensile rate of 5.0 × 10−4 m/sec. The direction of pulling the lead was 45° with respect to the PCB.

The appearance of the solder joint was examined using a microscope; the microstructural character of the solder joint was also examined using a scanning electron microscope.

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3. Results and Discussion

3.1 Joint reliability of Sn-Zn-Bi solder

3.1.1 The reflow process

The Sn-Zn-based solder shows high reactivity of Zn with Cu and forms a Cu-Zn reaction layer not found in Sn-Pb eutectic solder, which impairs joint properties at high temperatures. The Cu-Zn reaction layer clearly shows interfacial deterioration at $40^\circ$C/$125^\circ$C heat cycles, as shown in Fig. 1, but initiation of joint interfacial deterioration is seen even at $-40^\circ$C/$150^\circ$C heat cycles. Also, as shown in Fig. 2, Zn-O is formed at the joint interface under high-temperature ($85^\circ$C)/high-humidity (85%) conditions, impairing the interfacial quality.

Based on the facts as discussed, the Sn-Zn-based solder material requires examination of joint reliability and identification of applicable environments.

3.1.2 The reflow/wave mixed process

When using a two-step soldering process such as reflow soldering on one side of a board and wave soldering on the other side, the primary solder joints may delaminate during reheating for the secondary soldering. This phenomenon is particularly noticeable with high Bi-content solder (2~3 mass% Bi) and relatively large components (for example, 208-pin QFPs) with Sn-Pb electrode plating. Figure 3 shows the appearance and delaminated interfacial condition of a solder joint made with Sn-8Zn-3Bi solder in a reflow process on a Sn-Pb-plated lead of a 20 mm x 20 mm 120-pin QFP, which was then reheated to $145^\circ$C in a wave soldering process. The segregation of Bi and Pb in the joint interface forms a low melting-point compound phase. When the compound phase is heated above its melting point while the joint interface is already in a melted condition, board warp easily causes the interface to delaminate. The reason for the more marked separation seen in large components is that they are affected relatively more strongly by board warp.

As evidenced, delamination is believed to occur under the combined conditions in which component leads are Sn-Pb-plated and the reheating temperature exceeds the melting point of the low melting-point compound; the joint is then further affected by board warp.

For this reason, a reflow/wave solder mixed process requires a solder material that contains the smallest practical Bi content and suppresses generation of the low melting-point compound phase which has melting point of $96^\circ$C.

While working with a reflow soldering process or reflow/wave mixed soldering process that features the issues discussed above, we studied the solder joint properties of Sn-Ag-Bi-In solder, since, of the family of Sn-Ag-based solders known to have good mechanical properties, it contains the smallest quantities of Bi. The following section describes the joint characteristics of Sn-Ag-Bi-In solder, specifically of Sn-3.5Ag-0.5Bi-8In, which has the lowest melting point.
3.2 Basic properties of Sn-Ag-Bi-In solder

When lead-free solder is applied to joint forming, the reflow peak temperature needs to be maintained at the melting point $+10^\circ C.^{12}$ If component heat resistance is assumed to be 220 to 230$^\circ C$, the solder melting point needs to be around 210$^\circ C$. The properties of Sn-Ag-Bi-In solders are shown in Table 1. Addition of Bi is effective for lowering the melting point, whereas addition of In does not substantially affect elongation. Therefore, combined addition of Bi and In is effective for lowering the melting point.

Figure 4 shows the result of a joint strength evaluation made using Sn-Ag-Bi-In solder joints on a 0.5 mm pitch QFP with leads plated with Sn-Bi, Pd, and Sn-Pb. Every one of the solder types shows a joint strength comparable to or better than that of Sn-Pb eutectic solder.

3.3 Joint properties after thermal cycling

To examine the thermal cycle test characteristics of the Sn-Ag-Bi-In solder, a thermal cycle test was performed with a

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**Table 1 Basic physical properties of Sn-Ag-Bi-In solder.**

<table>
<thead>
<tr>
<th>Alloy composition (mass%)</th>
<th>Melting Temperature ($^\circ C$)</th>
<th>Tensile strength (kgf/mm$^2$)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solidus</td>
<td>Liquids</td>
<td></td>
</tr>
<tr>
<td>Sn-Ag-Bi-In</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bal.</td>
<td>3.5</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>Bal.</td>
<td>3</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Bal.</td>
<td>3.5</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Bal.</td>
<td>3.5</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>Sn-Pb</td>
<td>Bal.</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Sn-Zn-Bi</td>
<td>Bal.</td>
<td>3</td>
<td>8</td>
</tr>
</tbody>
</table>
cycle consisting of $-40^\circ C$ (30 min) followed by $125^\circ C$ (30 min) and $-40^\circ C$ (15 min) followed by $110^\circ C$ (15 min). The solder joint surface conditions of the Sn-3.5Ag-0.5Bi-8In, which has the lowest melting point of the Sn-Ag-Bi-In solder family, are shown in Fig. 5. A corrugated pattern appeared on the joint surface after 1000 cycles, whereas no significant changes in the surface condition were observed after 1000 cycles of a thermal cycle test at $-40^\circ C/110^\circ C$. This result suggests that a boundary exists, reflecting changes in surface conditions, between $110^\circ C$ and $125^\circ C$. To test for cracks in the fillet of the solder joint with a corrugated pattern, the cross-section was observed, with result shown in Fig. 6. No cracks were present, although some unevenness was seen on the joint surface.

The microstructure of a solder joint using Sn-3.5Ag-0.5Bi-8In solder was then observed. The results are shown in Fig. 7. The behavior of indium in the Sn-3.5Ag-0.5Bi-8In solder under the same conditions is shown in Fig. 8. In all types of solder, indium was dispersed over the entire Sn area of the fillet. After 1000 cycles, however, the Ag, which was initially dispersed in the Sn area, rose in concentration and formed a particle-shaped Ag-In substance. The particle size of the Ag-In compound phase was greater and more sparsely scattered in Sn-3.5Ag-0.5Bi-8In than in Sn-3.5Ag-0.5Bi-3In. We believe that the formation process of this Ag-In compound phase, combined with the thermal strain exerted by the thermal cycles, result in the surface corrugations seen on the joint surface. No segregation of this Ag-In compound was found in the joint interface.

The change in joint strength after the thermal cycle test of the Sn-3.5Ag-0.5Bi-8In is shown in Fig. 9. All combinations of different component lead plating showed joint strength comparable to that of Sn-Pb eutectic solder.

Based on the observations made in the thermal cycle test at $-40^\circ C$ (30 min)/$125^\circ C$ (30 min) for 1000 cycles, the Sn-3.5Ag-0.5Bi-8In solder, even with changes in the surface condition, showed sufficient joint strength and no cracks in the joint, proving quality comparable to Sn-Pb eutectic solder.

### 3.4 Joint properties after a high-temperature/high-humidity test

To examine the joint properties of the Sn-Ag-Bi-In solder under a high-temperature/high-humidity environment, the
<table>
<thead>
<tr>
<th>Sn-3.5Ag-0.5Bi-8In</th>
<th>-40°C(30min)/125°C(30min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
</tr>
</tbody>
</table>

Fig. 7 Microstructure of a QFP solder joint (Sn-3.5Ag-0.5Bi-8In).

Fig. 8 Behavior of Sn, Ag, In in the Sn-3.5Ag-0.5Bi-8In solder (−40°C (30 min)/125°C (30 min)).
Joint properties at 85°C/85%RH were evaluated by observing the surface condition of solder joints made on 0.5 mm pitch QFP leads with Sn-Bi plating, Pb plating and Sn-Pb plating. The result with the Sn-3.5Ag-0.5Bi-8In solder is shown in Fig. 10. A corrugated pattern appeared on the joint surface after 1000-hour exposure. This result was the same for all plating types.

The microstructure of solder joint under this set of conditions was observed, with the result shown in Fig. 11. The fillet surface showed corrugations, but no cracks were found. The indium phase initially dispersed in the Sn matrix of a fillet and formed an indium oxidized phase near the fillet surface after being left under the above conditions as well as Sn-Zn-based solder. The change in surface conditions is presumed to attributable to the presence of this indium oxidized phase. No generation of the indium oxidized phase was found in the joint interface at that time. Because no indium oxidized phase was found near the fillet surface after the thermal cycle test, the change in the fillet surface in the thermal cycle test and high-temperature/high-humidity test is presumed to occur by different mechanisms.

The change of joint strength of the Sn-3.5Ag-0.5Bi-8In solder in the high-temperature/high-humidity test is shown in Fig. 12. All combinations with different component lead plating showed joint strength comparable to that of Sn-Pb eutectic solder.

Based on the observations made in the environmental test of 85°C/85%RH for 1000 hours, the Sn-3.5Ag-0.5Bi-8In solder joint strength is shown in Fig. 9. Changes in Sn-3.5Ag-0.5Bi-8In solder joint strength after a thermal cycle test (−40°C (30 min)/125°C (30 min)).

<table>
<thead>
<tr>
<th></th>
<th>Sn-Bi plating</th>
<th>Sn-Pb plating</th>
<th>Pd plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000h</td>
<td></td>
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</table>

Fig. 10 Sn-3.5Ag-0.5Bi-8In solder joint, before and after 1000-hour exposure at 85°C/85%RH.

Fig. 11 Sn-3.5Ag-0.5Bi-8In solder joint structure after 1000-hour exposure at 85°C/85%RH.
solder, even with the change in its surface condition, showed sufficient joint strength and no cracks in the joint, thereby proving sufficient quality comparable to Sn-Pb eutectic solder.

3.5 Joint properties in a reflow/wave mixed process

The joint properties of the Sn-Ag-Bi-In solder under reheated conditions were examined. A 20 mm x 20 mm 120-pin QFP with 0.65 mm pitch leads plated Sn-Pb was reflow-soldered and the joints then reheated to a temperature above the presumed solidus temperature of Sn-Ag-Bi-In-Pb in the joint but below the liquidus temperature of the solder.

The solder joint made using Sn-3Ag-2.5Bi-2.5In, which has the highest Bi content of the Sn-Ag-Bi-In family, formed a low melting-point phase of Sn-Pb-Bi (melting point 96°C) as a result of reheating and caused delamination at the joint interface. The Sn-3Ag-0.5Bi-3In did not cause noticeable delamination, but the Sn-3.5Ag-0.5Bi-8In generated a minute separation. The result is shown in Fig. 13 for comparison with Sn-8Zn-3Bi solder. Observation of the Sn-3.5Ag-0.5Bi-8In joint interface did not find any low melting-point phase or evidence of remelting. This is because melting point of the Sn-3.5Ag-0.5Bi-8In added Pb doesn’t fall to less than 150°C. The Bi and In content were presumed to affect the formation of delamination. The measurement results for joint strength of Sn-3Ag-0.5Bi-3In and Sn-3.5Ag-0.5Bi-8In are shown in Fig. 14 in comparison with Sn-8Zn-3Bi solder. No significant deterioration of joint strength was observed with the Sn-Ag-Bi-In family containing 0.5 mass% of Bi. The possible growth of minute delamination of the Sn-3.5Ag-0.5Bi-8In was also examined using a thermal cycle test, but no growth trend was identified.

Based on the test results as described above, Sn-3.5Ag-0.5Bi-8In is believed to provide comparable joint properties to those of Sn-Pb eutectic solder when applied to reflow/wave mixed process boards.

4. Conclusion

The joint properties of the Sn-Ag-based low melting point solder, specifically the Sn-Ag-Bi-In solder family, were studied by means of a thermal cycle test, high-temperature/high-humidity test, and reheating by reflow/wave mixed process. The results are as follows.

(1) The joint strength of the Sn-Ag-Bi-In solder after a thermal cycle test and high-temperature/high-humidity test was equivalent to the joint strength of Sn-Pb eutectic solder.

(2) The joint surface condition of the Sn-3.5Ag-0.5Bi-8In solder changed after the thermal cycle test and high-temperature/high-humidity test, but no crack generation and no
effect on joint strength were confirmed.

(3) Joint interfacial delamination after reheating in the reflow/wave mixed process was observed in the Sn-3Ag-2.5Bi-2.5In solder, which contained relatively high levels of Bi. Minute delaminations were observed in the Sn-3Ag-0.5Bi-8In solder but no extension of the delamination was confirmed after the thermal cycle test.

(4) The joint reliability of the Sn-Ag-Bi-In solder is comparable to that of Sn-Pb eutectic solder, thereby making this solder a potential candidate for extension of the lead-free circuit manufacturing process.

REFERENCES