Effects of a Third Element on Microstructure and Mechanical Properties of Eutectic Sn–Bi Solder

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Abstract
The effects of a third element, namely silver, copper, zinc, or antimony, on the microstructure and mechanical properties of eutectic tin-bismuth (Sn–Bi) solder were investigated. The investigation showed that, except for zinc, the addition of a trace amount of the third element improves the ductility of the Sn–Bi solder owing to the formation of a fine, homogeneous ternary eutectic microstructure. In particular, the antimony addition is the most effective in improving solder ductility. That is to say, the addition of 0.5 wt% antimony minimizes the grain size of the eutectic microstructure and increases the elongation up to about 40%. Moreover, an intermetallic compound, namely, SnSb, precipitated finely from the solid tin solution near the grain boundaries with bismuth. This fine precipitated intermetallic compound suppresses the coarsening of the eutectic structure and thus improves solder ductility.

Keywords: Sn–Bi Solder, Low Melting Point, Third Element, Microstructure, Mechanical Property

1. Introduction
For connecting circuit boards and substrates, several kinds of bonding materials and technologies — which aim to extract the utmost performance from high-performance semiconductor devices — are available. As a key material for such bonding, solder-alloy metals have been used for many years now. In view of environmental regulations, tin-silver-copper (hereafter, “Sn–Ag–Cu”) is presently used as such a solder-alloy material because it does not contain lead. Sn–Ag–Cu solder, however, has a higher melting point than that of conventional eutectic tin-lead (Sn–Pb) solder. The temperature of solder bonding is therefore also higher. Consequently, on soldering, components and substrates need greater heat resistance than that possible up until now. In addition, the dangers connected with a number of problems (such as increased thermal stress during soldering) arise. Given that miniaturization and densification of electronic products will continue in the future, it is necessary to establish a low-temperature packaging process that exerts a low thermal load on packaging components and their surroundings. It is therefore necessary to develop a low-melting-point solder that can make this process possible.[1] Furthermore, the application of this low-melting-point solder should reduce energy consumption due to the reduction in heating temperature.

Eutectic tin-bismuth (Sn–Bi) solder has a lower melting point (139°C) than that of eutectic Sn–Pb solder (183°C); thus, it is a promising material for soldering at temperatures lower than hitherto possible. At the same time, however, owing to the hard, brittle quality of bismuth, Sn–Bi solder is inferior in terms of ductility.[2] Aiming to address this problem, Suganuma, et al.[3] and McCormack, et al.[4] investigated improving Sn–Bi ductility by adding minute amounts of silver as a ternary element. Moreover, our own previous study yielded similar results.[5] However, a solder with an added trace of silver, hereafter referred to as “Sn–Bi–Ag solder,” is not expected to have enough ductility in response to impact stress under a high strain rate (see Fig. 1). In the present study, focusing on Sn–Bi solders with an additional third element other than silver (namely, copper, zinc, or antimony), the authors have identified the influence of the microstructure of the solder on its ductility.

2. Concept of a Third Element
In general, the addition of trace amounts of elements to a metal can change the solidification structure of the metal.
and thus modify its mechanical properties. In the present investigation, three trace elements — namely, copper, zinc, or antimony — were added to Sn–Bi solder. Among those three elements, copper and antimony behave in a similar manner to silver, and they do not form intermetallic compounds with bismuth but do so with tin instead. Although copper and silver make a eutectic reaction with bismuth, antimony forms a complete solid-solution system with bismuth. Furthermore, it is known that zinc does not form intermetallic compounds with either tin or bismuth. Given these facts, the structure formed after a solder hardens will differ according to the particular element added to the solder-alloy (see Table 1).

In light of the above, assuming Sn–Bi–Ag solder as the conventional technology, we have investigated the effects of the third element on the microstructure and mechanical properties of eutectic Sn–Bi solder.

3. Experiments
3.1 Specimen

The compositions of the solders used in the investigation are listed in Table 2. Each solder was made by melting Sn–58wt%Bi at 200°C and then adding the third elements (silver, copper, zinc, or antimony) using RA-type flux. The dimensions and appearances of the test pieces used for tensile testing are shown in Fig. 2. The molten solders were cast in a silicone mold, and hardened by cooling at a rate of 1°C/s, which is close to the actual reflow cooling conditions.

3.2 Tensile test

Tensile tests were carried out on a universal material testing machine (INSTRON 5505) at a tension rate of 3 mm/min (i.e., a strain rate of $2.0 \times 10^{-3} /s$). Each test piece was tested at room temperature until complete fracture occurred.

![Fig. 1 Ductility of Sn–Bi solder under high and low strain rate improved by silver addition.](image)

![Fig. 2 Size of test piece for tensile test.](image)

### Table 2  Solder materials.

<table>
<thead>
<tr>
<th>Solders</th>
<th>Elements (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn–Bi</td>
<td>Sn 42  Bi 58  Ag None  Cu None  Zn None  Sb None</td>
</tr>
<tr>
<td>Sn–Bi–Ag</td>
<td>Sn 41.8  Bi 57.7  Ag 0.5  Cu None  Zn None  Sb None</td>
</tr>
<tr>
<td>Sn–Bi–Cu</td>
<td>Sn 41.8  Bi 57.7  Ag None  Cu 0.5  Zn None  Sb None</td>
</tr>
<tr>
<td>Sn–Bi–Zn</td>
<td>Sn 41.8  Bi 57.7  Ag None  Cu None  Zn 0.5  Sb None</td>
</tr>
<tr>
<td>Sn–Bi–Sb</td>
<td>Sn 41.8  Bi 57.7  Ag None  Cu None  Zn None  Sb 0.5</td>
</tr>
</tbody>
</table>

### Table 1  Affinity of third elements with Sn and Bi, and expected effect for improvement of solder ductility.

<table>
<thead>
<tr>
<th>Base solder element</th>
<th>Third elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>IMC formed</td>
</tr>
<tr>
<td>Bi</td>
<td>Solid immiscible Eutectic point present</td>
</tr>
<tr>
<td>Expected effect of addition</td>
<td>Ternary eutectic IMC precipitation</td>
</tr>
</tbody>
</table>

IMC: Intermetallic Compound
ture. After the tensile testing, the gauge length of each fractured test piece was measured, and the elongation at fracture was calculated. The tensile test result was statistically averaged over three trials.

### 3.3 Microstructural analysis

The microscopic structure of each solder test piece was observed with a scanning electron microscope (SEM), and each constituent phase of the solder was identified with an electron-probe microanalyzer (EPMA). The average grain size of the eutectic structure was measured in terms of the number of grains per unit area in a photomicrograph. In addition, equilibrium diagrams for each solder were determined using standard software (“Pandat5.0,” CompuTherm LLC) run in conjunction with a thermal-dynamics database (“ADAMIS,” Alloy Database for Micro-Solder).

### 4. Results and Discussion

#### 4.1 Mechanical properties of Sn–Bi with added third element

Tensile tests were performed on each solder, namely, eutectic Sn–Bi with 0.5 wt% trace-element addition (silver, copper, zinc, or antimony), and the test results plotted in Figs. 3(a) and (b). In regards to tensile strength, there are no major differences between any of the solders with the added elements (Fig. 3(a)). On the other hand, as shown in Fig. 3(b), the breaking elongation tends to improve with the addition of the third elements except for zinc. In particular, the solder material with 0.5 wt% antimony addition shows a much larger breaking elongation (40%) than the solder materials with the other third-element additions (from 10% to 20%). It is thus clear that the antimony addition is the most effective for improving solder ductility.

#### 4.2 Microstructure of Sn–Bi with added third element

To investigate the effect of each third element on the solder microstructure, SEM observations were carried out, and the precipitation patterns of solders (with eutectic structure and/or added elements) were compared. The obtained SEM images are shown in Fig. 4. The average grain sizes of the eutectic structure determined from the SEM images are shown in Fig. 5. While the eutectic Sn–Bi solder shows a microstructure composed of tin (dark regions in the micrograph) and bismuth (white regions), in the Sn–Bi–Ag solder with 0.5 wt% silver addition, a new intermetallic compound, namely, Ag₃Sn, is formed. Although not that much Ag₃Sn precipitates when the amount of added silver is extremely low, it is known that if
the amount of silver added is more than 1 wt%, the Ag<sub>3</sub>Sn regions will grow and the solder ductility will degrade. Similarly, in the case of added copper, the fine Cu<sub>6</sub>Sn<sub>5</sub> intermetallic compound is dotted about, and some coarser regions (several tens of microns in size) are seen.

On the other hand, in the Sn–Bi solder with added zinc (Sn–Bi–Zn), needle-like zinc can be seen in the eutectic Sn–Bi structure. Given that the added zinc has no recognizable effect on the eutectic Sn–Bi structure, it is speculatively concluded that neither tin nor bismuth is able to form an intermetallic compound with zinc. Moreover, for the solder with 0.5 wt% antimony addition, an extremely fine eutectic structure — which is not seen in the case of the other added elements — can be seen. Moreover, precipitation of coarse intermetallic compound like that seen in the case of the silver and copper additions cannot be seen.

Although it is thought that the added antimony is present in both the tin and bismuth structures, antimony, in particular, does not really form a solid solution in tin, so it is thought to exist as a SnSb intermetallic compound. As for the 0.5 wt% trace-element addition, since the existence of antimony could not be confirmed, the state of the microstructure under a 1 wt% excess-element addition was observed, and the behavior of antimony was inferred from that. The structure of the Sn–Bi–Sb solder (with 1 wt% antimony addition) and the EPMA results are shown in Fig. 6. The images confirm that the antimony exists in the form of sub-micron-order particles, and the SnSb intermetallic compound is dispersed in the tin phase near the grain boundaries of the eutectic structure. It is speculated that this precipitation of fine SnSb intermetallic compound near the grain boundaries of tin and bismuth is strongly involved in suppressing the coarsening of the eutectic structure. These results show that finer grain size results in higher elongation.

4.3 Mechanism of microstructure formation discussed by using ternary phase diagram

4.3.1 Sn–Bi solder with added silver

It has been reported that the best ductility can be obtained under a composition of 0.5 wt% silver added to a eutectic Sn–Bi alloy. According to the tensile-test results obtained in the present study, the ductility of Si–Bi solder with added silver is improved compared to eutectic Si–Bi solder (see Fig. 3(b)). To investigate the factors contributing to this improvement in ductility, the ternary phase diagrams for (Sn–57Bi)<sub>1</sub>–y–Ag<sub>y</sub> (i.e., 57 wt% bismuth) with various ratios (y = 0–6 wt%) of added silver were calculated (see Fig. 7). The phase diagram shows that a ternary-eutectic reaction occurs at around 0.5 wt% silver addition. It is considered that as a result of Ag<sub>3</sub>Sn crystallizing in the eutectic structure, coarsening of the solder structure is suppressed and solder ductility is thereby improved by effects such as grain-boundary slipping. Moreover, it is known that as the degree of supercooling under
the cooling conditions increases, the eutectic structure gets finer. Since the ternary eutectic is thermodynamically stable in the liquid state (as is also shown by the lowering of the melting point), the ternary eutectic is easier to form on further supercooling than a binary eutectic. This means that when forming a ternary eutectic by adding silver, even under slow cooling rates like those used in packaging, supercooling occurs more easily, and a fine structure (which has the effect of improving ductility) can be obtained.

4.3.2 Sn–Bi solder with added copper
As in the case of added silver described in Section 4.3.1 above, the ternary phase diagram for \((\text{Sn–57Bi})_{1–\gamma}–\text{Cu}_y\) with the ratio \((\gamma = 0–6 \text{ wt%})\) of added copper was calculated (see Fig. 8). It is clear that by adding copper, a ternary eutectic reaction — forming \(\text{Sn–Bi–Cu}_6\text{Sn}_5\) — occurs. This reaction forms by a similar mechanism to that which generates the \(\text{Sn–Bi–Ag}_3\text{Sn}\) ternary eutectic with the addition of silver, and it is speculated that it is a contributing factor to the improvement of ductility. Furthermore, compared to \(\text{Ag}_3\text{Sn}, \text{Cu}_6\text{Sn}_5\) is not so hard and brittle. As for this characteristic, it is clear from Fig. 3 (a) that the tensile strength of \(\text{Sn–Bi–Cu}\) solder with added copper is lower than that of \(\text{Sn–Bi–Ag}\) solder with added silver. This fact is considered to be a contributing factor to the superior ductility of \(\text{Sn–Bi–Cu}\) solder compared to \(\text{Sn–Bi–Ag}\) solder.

On the other hand, the ternary eutectic \(\text{Sn–Bi–Cu}\) structure is on the \(\text{Sn–Bi}\) side in comparison to the silver-addition case, and it is necessary to take note of the point at which the liquidus line rises exponentially. This is a hazardous property that affects the fusibility of the solder itself. What is more, as the solid-liquid coexistence region expands, coarsening of the primary crystal of the grown \(\text{Cu}_6\text{Sn}_5\) intermetallic compound is quite possible.

4.3.3 Sn–Bi solder with added zinc
As for the \(\text{Sn–Bi–Zn}\) solder (i.e., 0.5wt% zinc addition), in comparison with the other element additions, though a slight coarsening of the crystal structure was observed, the ductility was not degraded. The ternary phase diagram for \((\text{Sn–57Bi})_{1–\gamma}–\text{Zn}_y\) with the ratio \((\gamma = 0–6 \text{ wt%})\) of added zinc was calculated (see Fig. 9). When zinc is added, as in the case of the silver and copper additions, a ternary eutectic composed of \(\text{Sn–Bi–Zn}\) is formed. Moreover, the eutectic structure is on the zinc-rich side compared to the silver- and copper-addition cases. Accordingly, it is supposed that if the zinc addition is below 3 wt%, coarsening of the zinc occurs less readily. Furthermore, in the actual observations of the \(\text{Sn–Bi–Zn}\) structure, primary tin crystal (which was seen in patches in the \(\text{Sn–Bi}\) eutectic solder) was virtually unseen — as in the cases of the other added elements.

Although the refining of the eutectic structure with added zinc was not detected, the above fact (i.e., lack of primary tin crystal) is thought to be a contributing factor in assuring the same ductility as the eutectic \(\text{Sn–Bi}\) solder. Moreover, in regards to zinc crystallizing as needles in the structure of the zinc-added solder, the same phenomenon was reported to occur in the \(\text{Sn–8Zn–3Bi}\) solder.[8] Although the reason for this phenomenon is still unclear, it is speculated that it is probably due to the inherent nature of elemental zinc.

4.3.4 Sn–Bi solder with added antimony
The ternary phase diagram for \((\text{Sn–57Bi})_{1–\gamma}–\text{Sb}_y\) with the ratio \((\gamma = 0–6 \text{ wt%})\) of added antimony was calculated (see Fig. 10). Focusing on the case of the 0.5 wt% antimony addition, it is clear that the melting point is \(141.6^\circ\text{C}\). When
the temperature decreases, the solid-solubility limit of antimony in tin falls, and antimony exceeding the limit precipitates as SnSb. Fine SnSb (like that shown in Fig. 4) precipitates near the grain boundaries of the tin, and this precipitation is thought to be a contributing factor to the refining of the microstructure.

When the antimony addition is increased to the 1.0-to-5.0 wt% range, primary bismuth crystal forms easily. In addition, when it exceeds 5 wt%, it is supposed that SnSb becomes the primary crystal and ductility is degraded. Furthermore, the increase in the addition of antimony broadens the solid-liquid coexistence region, so bismuth or coarse SnSb crystallize more easily. Consequently, it is considered that the addition of a small amount of antimony (that is, a mere 0.5 wt%) — which crystallizes as a fine SnSb intermetallic compound and suppresses coarsening of the eutectic structure — is favorable for a significant improvement in ductility.

5. Summary

The results of this study regarding adding a third element to eutectic Sn–Bi solder, investigating the resulting ductility, and observing the microstructures can be summarized as follows. The addition of a third element increases the liquidus temperature and makes the formation of intermetallic compounds or primary crystals of the added element more likely. When the added element is silver or copper, coarse primary crystals of intermetallic compound grow even when the amount of the added element is extremely low (i.e., 0.5 wt%). This result means that the risk of degrading ductility is high even if the eutectic structure is fine. On the other hand, with antimony, if the amount added is less than 1 wt%, although the liquidus temperature is raised, generation of SnSb is thought to be by precipitation, not crystallization, so the coarse primary crystal — like that occurring with the other added elements — does not occur readily. It is thought that suppressing the solidification structure in this manner is a factor in the extremely large improvement in ductility that occurs with the addition of antimony.

References