Effect of Au addition on Microstructural and Mechanical Properties of Sn–Cu Eutectic Solder

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The effect of Au addition on the microstructural and the tensile properties of Sn–0.7 mass%Cu alloy was examined. Tensile strength and 0.2% proof stress remarkably increase up to 0.3 mass%Au primarily due to solid solution hardening. Beyond 0.3 mass%Au, due to precipitation of large intermetallic compounds, elongation decreases while tensile strength and 0.2% proof stress increase slightly. With Au addition to Sn–Cu binary alloy, the eutectic endothermic peak in DSC, i.e., the melting reaction at 227 °C, becomes broader and shifts to the lower temperature range. With Au beyond 2 mass%, the broad peak becomes smaller splitting into two peaks and moving towards lower temperature while a new peak appears at about 212 °C. These thermal reactions can be well explained by the formation of β-Sn, Cu₆Sn₅ and AuSn₄ with Au more than 1 mass%. EPMA observation revealed that much amount of Au and Cu dissolve into Cu₆Sn₅ and AuSn₄, respectively.

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1. Introduction

Owing to environmental and health concerns from the toxicity of Pb, much work has been carried out to find a new solder alloy as replacement of the most commonly used Sn–Pb solder.1–8) Due to the processing requirements and the soldering operational environment, the compositions of suitable solders are different from one application to another. For these reasons, Sn-based multi-component alloys with alloying elements such as Ag, Bi, Zn and Cu are likely to be most promising.9, 10) Although many alloys designed with lead-free elements exist, none meets all standards. Therefore, in order to develop proper alloy compositions for the new solder systems, one should consider various properties of the candidate alloy systems, such as material properties, i.e. physical, chemical and mechanical properties, as well as cost and manufacturability.

Among various properties, one of the major concerns is economy for consumer products. Sn–Cu eutectic alloy has the great advantage in cheapness. This benefit is in fact promoting the adoption of Sn–Cu alloys for wave soldering in the mass-production of commercial electronics. Nevertheless, the Sn–Cu eutectic alloy is known to have poor mechanical properties compared with other lead-free solders and even with Sn–Pb solder.1, 4) In order to ensure the reliability of electronic circuits soldered with Sn–Cu alloy, one needs to improve its mechanical properties by some microstructural control. One of the most promising methods to improve the mechanical properties of metallic materials is the fine dispersion of a stable third phase in the matrix. In the previous work,11) the authors reported the effect of Ag addition on the microstructural and mechanical properties of Sn–Cu eutectic alloy. In the previous work,12, 13) the authors reported that both the microstructure and phase change can significantly influence the mechanical properties by some microstructural control. In contrast to Ag, Au can dissolve in the β-Sn matrix up to about 0.3 mass%Au at 200 °C.14) These facts imply that a small amount of Au addition to Sn–Cu can improve the mechanical properties by solid solution hardening and as well as by dispersing the Sn–Au–Cu intermetallic compound in the matrix. Thus, the purposes of this paper are to investigate the effect of Au addition to Sn–Cu eutectic alloy both on microstructural and tensile properties and to find out the best Au composition that gives a reliable Sn–Cu solder alloy.

2. Experimental Procedure

Cast ingots of Sn–0.7 mass%Cu (hereafter, called as Sn–0.7Cu) and of Sn–0.7Cu with 0.1, 0.3, 0.5 and 1 mass%Au were used in this work. For thermal analysis, two additional alloys, 2 mass%Au and 3 mass%Au were prepared. These alloys where prepared from pure Sn (99.9% pure), pure Cu (99.99% pure) and pure Au (99.95% pure). The alloys were melted in a crucible, stirred at 400 °C for 2 to 3 h. Tensile specimens of the alloys were re-melted at 300 °C for 30 min and were cast into a steel mold. Figure 1 shows (a) the temperature changes of an ingot specimen as a function of time during casting and (b) the illustration of a tensile specimen cut from the ingot. Ingots were cooled to room temperature within 30 s and the temperature difference at different points in each ingot was quite small. In the actual production of electronic circuit boards, soldered joints are cooled in a few tens of seconds to 1 min depending on the geometry of the assembly structure. The current solidification condition seems to lie within a reasonable cooling rate range. Tensile specimens have a gauge section of 46 mm in length, 8 mm in width and 1 mm in thickness. These specimens were polished with 0.3 μm Al₂O₃ particles. All specimens were heat-treated at 100 °C for 30 min to remove residual stress and defects induced during preparation. Tensile tests were carried out at strain rates of 3.47 × 10⁻⁴ s⁻¹ at room temperature. For one data, more than eight samples were tested.

The thermal reaction of the solder alloys was recorded by differential scanning calorimetry (DSC) on heating. DSC was carried out by using small pieces of alloys about 20 mg in weight at heating rates of 0.5°C/min and 3°C/min from room temperature to 300°C in an Ar gas flow. However, in the
In the present experiments, data plotted at 0.5°C/min are more sensitive than that at 3°C/min. Therefore, DSC profiles are performed on 0.5°C/min of the two heating rates. Before measurement, the temperature was calibrated by using pure In as a standard. From the DSC measurements, several endothermic reaction peaks were obtained.

For the observation of microstructure, specimens were polished with 0.3 μm Al₂O₃ powders and were etched slightly in ethanol-5 vol% hydrochloric acid. The Image Hyper II Image Analyzer was employed to measure the area fraction of the interdendritic eutectic and AuSn₄ intermetallic compound and the average and standard deviation values of 20 fields under magnifications of ×200 and ×5000 for each specimen were recorded. The magnification of ×200 used for image analysis of the interdendritic eutectic contains more than 80 β-Sn dendrites, i.e., photographs of Fig. 3, that of ×5000 used for AuSn₄ more than 40% fraction of interdendritic eutectic.

Observation was carried out by optical microscopy (OM) and scanning electron microscopy (SEM). The element distribution was examined by electron probe microanalysis (EPMA). X-ray diffraction was also used to identify phases appearing in the alloys.

### 3. Results and Discussion

#### 3.1 Microstructure evolution by Au addition

Figure 2 shows the schematic illustration and optical micrographs at various positions in the as-solidified Sn–0.7Cu specimen. The microstructure consists of both columnar and equiaxed matrix structures, which is commonly referred as typical ingot type of structure. The columnar grain morphology may primarily be attributed to the initiation of primary β-Sn phase solidification predominantly at the mold wall as a result of heterogeneous nucleation. On the other hand, the morphology apart from the sample edge almost consists of equiaxed β-Sn grains.

The typical OM photographs of the as-solidified alloys with varying Au content are shown in Fig. 3, in which the morphologies having equiaxed matrix structures for each alloy are enlarged. The microstructure of binary eutectic Sn–0.7Cu consists of two regions, i.e., the dendrite arm surrounded by the interdendritic eutectic. In the previous work, it was identified that the dendrite arm is primary β-Sn phase while the interdendritic eutectic is the Cu₅Sn/β-Sn eutectic phase. Without the addition of Au, the size of the β-Sn dendrite is about 30 to 50 μm. The width of the interdendritic eutectic varies from position to position and the largest width is about 10 to 20 μm. By increasing Au content up to 0.5%, no significant change was observed in microstructure. With the addition of 1% Au, the width of the interdendritic eutectic decreases. Figure 4 shows the change of the fraction of the interdendritic eutectic as a function of Au content. The fraction of interdendritic eutectic area gradually decreases as increasing Au.

With 1% Au, AuSn₄ was identified in addition to these two phases by X-ray diffraction analysis. AuSn₄ was not detected below 1% Au alloys possibly because the amount is too little for the detection by X-ray diffraction. Figure 5 shows SEM images of Sn–0.7Cu alloys with 0.3Au, 0.5Au and 1Au. Combined with EPMA analysis, it was found that the interdendritic eutectic is composed of intermetallic Cu₆Sns,
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3.2 Influence of Au on tensile property

Figure 8 shows the effect of Au content on tensile strength, 0.2% proof stress and the elongation of Sn–Cu–Au solders. Tensile strength and 0.2% proof stress increase with increasing Au up to 0.3 mass%. Elongation also remarkably increases with increasing Au up to 0.3 mass%. It is interesting fact that elongation is improved at the same time of strength increase by the addition of Au up to 0.3 mass%. In the Au content from 0.3 mass% to 0.5 mass%, tensile strength and 0.2% proof stress change little and slightly increase over 0.5Au up to 1 mass%Au. In contrast, elongation remarkably decreases when Au exceeds 0.3 mass%.

The strength increase in the Au range between 0 and 0.3 mass%Au can be explained by solid solution and/or dispersing hardening of Sn–Au fine compounds, which could not be identified in the present work. But beyond 0.3 mass%Au,
tensile strength and 0.2% proof stress exhibited little change while elongation decreases due to the formation of large AuSn₄ precipitation in the interdendritic eutectic. The area fraction of AuSn₄ in the interdendritic eutectic increases with increasing Au as is illustrated by Fig. 6. The increase of AuSn₄ and decrease of the interdendritic eutectic area also seem to influence the strength change.

Thus, from the mechanical properties change by the addition of Au, it can be said that the 0.3 mass% Au addition is the best composition for Sn–Cu eutectic alloy to improve both strength and elongation.

3.3 Thermal reaction

Figure 9 shows the DSC profiles of Sn–Cu solder alloys with Au on heating. Sn–0.7Cu exhibits one sharp endothermic peak at the binary eutectic temperature, 227.3°C, which indicates that the alloy melts completely at the eutectic temperature. With increasing Au content, this peak becomes broader and shifting towards lower temperatures. For Sn–0.7Cu–0.5Au, there is the main endothermic peak at 226.5°C with onset temperature at around 222.3°C. For Sn–0.7Cu–1Au, the main endothermic peak moves to a lower temperature at approximately 224.9°C and the onset temperature appears at around 216.8°C. Thus, by the Au addition to Sn–Cu binary alloy, the eutectic endothermic peak becomes broader as well as shifting to lower temperatures. In addition, by increasing the Au content, onset temperature appears at lower temperature.

Sn–0.7Cu alloys with beyond 2 mass% Au exhibit three endothermic peaks. For Sn–0.7Cu–2Au, the peaks are a small initial peak at 211.8°C, the second broad peak at around 223.5°C, and the last smallest peak at approximately 224.5°C. For Sn–0.7Cu–3Au, the initial peak on heating is larger than that of Sn–0.7Cu–2Au but the temperature is almost the same. On the other hand, the two peaks in the higher temperature range shift to lower temperatures than those of Sn–0.7Cu–2Au.

The endothermic peaks obtained for each alloy are summarized in Table 1 with each possible reaction scheme. The endothermic peak for the Sn–0.7Cu alloy is at 227.3°C, which is the eutectic temperature. In 0.5 and 1 mass% Au, solidus points are $T_{\text{es1}}$, i.e., 222.3°C and 216.8°C, liquidus points are 226.5°C and 224.9°C, respectively. In 2 and 3 mass% Au, solidus points are 1st peaks, i.e., 211.8°C and 211.9°C, liquidus points are 3rd peaks, i.e., 224.5°C and 222.5°C as is illustrated by Table 1. If Au is added more, solidus and liquidus point will be fixed and decreased, respectively. This trend seems to be continued up to ternary eutectic composition, and ternary eutectic point of Sn–Cu–Au system seems to be about 212°C.

By summarizing the results, with the Au addition to Sn–0.7Cu, the eutectic endothermic peak, i.e., the melting reaction at 227.3°C, becomes broader and shifting to lower temperature. And beyond 2 mass% Au, the broad peak becomes smaller splitting into two peaks and moving towards lower temperature while a new peak appears at about 212°C. Roeder has revealed a solidification reaction scheme for the Sn-rich part of the Au–Cu–Sn system. He found that the ternary eutectic point for the Sn-rich part of the Sn–Cu–Au system was observed at 211°C by using DSC.

Figure 10 shows SEM images of Sn–0.7Cu–2Au and Sn–0.7Cu–3Au alloys. Combined with EPMA analysis, it was found that the interdendritic eutectic consists of the β-Sn/Cu₆Sn₅ binary eutectic and β-Sn/Cu₆Sn₅/AuSn₄ ternary eutectic phases. These phases were appeared by the two reaction schemes of (1) Liquid ↔ (Sn) + Cu₆Sn₅ (221.7, 223.5°C) and (2) Liquid ↔ (Sn) + Cu₆Sn₅ + AuSn₄ (211.8, 211.9°C), respectively. Figure 11 shows a liquids projection for the partial Au–Cu–Sn system. Bochvar and Liberrro, and Roeder reported that the ternary eutectic reaction, i.e., Liquid ↔ (Sn) + Cu₆Sn₅ + AuSn₄, appears at 211°C. They also reported that 8 at% Au dissolves in the Cu₆Sn₅ phase by about at 170°C and that Cu can exhibit a large solubility in AuSn₄. On the other hand, Keller has reported the formation of Cu₆AuSn₅ in a Mod I soldered terminal connection though the precise composition of this phase was not measured quan-
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SEM and EPMA element mapping images of (a) Sn–Cu–0.3Au and (b) 0.5Au alloys.

4. Conclusion

The present study examined the effect of Au addition on the microstructural and tensile properties of Sn–0.7Cu to improve mechanical properties. The results are summarized as follows:

1. By increasing Au content up to 0.3%, the microstructure of Sn–0.7Cu alloy does not show any apparent change. With 1 mass% Au addition, the size of primary β-Sn dendrite becomes somewhat smaller and the width of the interdendritic eutectic decreases.

2. Tensile strength and 0.2% proof stress remarkably increase up to 0.3 mass% Au. Beyond 0.3 mass% Au, elongation decreases while tensile strength and 0.2% proof stress increase slightly. The strength and elongation change is attributed to the area fraction change of the interdendritic eutectic with AuSn₄ and Cu₆Sn₅.

3. With the Au addition to Sn–Cu binary alloy, the binary eutectic endothermic peak, i.e., that at 227.3°C, becomes broader and shifts to lower temperature. With beyond...
Table 1  Endothermic peak temperatures (°C) and reaction scheme.

<table>
<thead>
<tr>
<th>Solders</th>
<th>1st peak</th>
<th>2nd peak</th>
<th>3rd peak</th>
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<tbody>
<tr>
<td>Sn–0.7Cu</td>
<td>—</td>
<td>—</td>
<td>227.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Liq. ↔ (Sn) + Cu₆Sn₅</td>
</tr>
<tr>
<td>Sn–0.7Cu–0.5Au</td>
<td>—</td>
<td>—</td>
<td>226.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T_onset: 222.3</td>
</tr>
<tr>
<td>Sn–0.7Cu–1Au</td>
<td>—</td>
<td>—</td>
<td>224.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T_onset: 216.8</td>
</tr>
<tr>
<td>Sn–0.7Cu–2Au</td>
<td>211.8</td>
<td>223.5</td>
<td>224.5</td>
</tr>
<tr>
<td>Sn–0.7Cu–3Au</td>
<td>211.9</td>
<td>221.7</td>
<td>222.5</td>
</tr>
</tbody>
</table>

Remarks (Reaction scheme)

|                  | Liq. ↔ (Sn) + Cu₆Sn₅ + AuSn₄ | Liq. ↔ (Sn) + Cu₆Sn₅ | Liq. ↔ (Sn) + Liq. |

Fig. 9  DSC profiles obtained from as-solidified Sn–0.7Cu alloys without Au, with 0.5Au and with 1Au. DSC profiles obtained from as-solidified Sn–0.7Cu alloys with 1Au, with 2Au and with 3Au. (continued).

2 mass%Au, the broad peak becomes smaller splitting into two peaks and moving to lower temperature while a new peak appears at 212°C.

(4) Only Cu₆Sn₅ and AuSn₄ are identified as the intermetallic phases. Much amount of Au and Cu dissolve into Cu₆Sn₅ and AuSn₄, respectively.

Fig. 10  SEM micrographs of Sn–Cu alloys (a) with 2Au and (b) with 3Au.

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REFERENCES

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Fig. 11 Liquidus surface projection for ternary Au–Cu–Sn systems.\(^\text{17}\)

<table>
<thead>
<tr>
<th>Reaction scheme</th>
<th>Phases</th>
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<tbody>
<tr>
<td>U6: Liq. + δ ↔ η + ε</td>
<td>δ → AuSn</td>
</tr>
<tr>
<td>U7: Liq. + e1 ↔ η1 + η1</td>
<td>η1 → AuCuSn or AuCuSn2</td>
</tr>
<tr>
<td>E1: Liq. ↔ ε + η + η1</td>
<td>ε → AuSn</td>
</tr>
<tr>
<td>E2: Liq. ↔ η + η1 + (Sn)</td>
<td>η1 → CuSn</td>
</tr>
<tr>
<td>P1: Liq. + e1 + η ↔ η1</td>
<td>η1 → CuSn</td>
</tr>
</tbody>
</table>