The thermal characteristics of various Sn-based solder alloys and intermetallic compounds (IMCs) formed at the Sn-9Zn-0.5Ag/Cu interface have been investigated by using differential scanning calorimetry, X-ray diffractometry, scanning electron microscopy, energy dispersive spectrometry, transmission electron microscopy and electron diffraction. The melting ranges of the Sn-37Pb, Sn-9Zn and Sn-3.5Ag alloys are 179.5–191.0, 195.5–208.1 and 220.4–227.8°C, and the heats of fusion are 104.2, 163.9 and 151.0 J/g, respectively. When 0.5 mass% Ag is added to the Sn-9Zn alloy, the melting temperature of the solder alloy increases from 195.5 to 196.7°C, but the melting range and heat of fusion decrease from 12.6 to 11.3°C and 163.9 to 74.7 J/g, respectively. The IMCs formed at the Sn-9Zn-0.5Ag/Cu interface are determined as a scallop-shaped Cu₆Sn₅ near the solder alloy, a flat Cu₉Zn₈ close to the Cu substrate and Ag₅Sn particles between the Cu substrate and Cu₅Zn₆ layer. The Cu₆Sn₅ is bi-structural, namely, hexagonal and monoclinic, which is caused by the Ag dissolution in the Cu₆Sn₅ layer.

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**Keywords:** thermal characteristics, intermetallic compounds, melting point, fusion heat, bi structure

1. Introduction

The Sn-37Pb eutectic solder alloy has been used widely as an interconnecting material in electronic packaging industry, but is a source for lead pollution.1,2) The major electronic industrialized countries such as Japan, Europe, and the United States of America have created up a roadmap in limiting the use of Sn-37Pb alloy since 2001.3-5) Even Japan has established strict regulations to ban Pb-contaminated imports.6) Therefore, the development of lead-free solders is one of the urgent subjects for the electronics industry.

The metallurgical characteristics of the Sn-37Pb solder alloy have been studied intensively.7-9) The Sn-9Zn and Sn-3.5Ag are the two important binary lead-free solders investigated,10,11) but inferior wettability and oxidation resistance of the Sn-9Zn alloy and high melting point (221°C) of the Sn-3.5Ag alloy, limit the usage of these solder alloys.12-15) Chen et al.16) have determined the melting and solidification characteristics of various solder alloys using DSC. Besides the binary alloys, ternary solder alloys are also considered as a substitute for the Sn-37Pb solder alloy. The suitable eutectic composition of the Sn-Ag-Cu solder alloy has been determined as 3.5 mass% Ag, 0.9 mass% Cu and the balance Sn by Loomans and Fine,17) but the melting point of the solder alloy is 217°C which is too high to use in practice. Yoon et al.18) has been investigated phase equilibrium in the Sn-Bi-In system. However, there are few lead-free solders which can substitute Sn-37Pb completely. Hence, the need to build a database of lead-free solders is urgent.

It has been shown that adding Ag to the Sn-9Zn solder alloy can improve wettability between the solder alloy and the Cu substrate by Takemoto et al.,19) because the addition of Ag reduces the potential difference between the base metal and the solder alloy. Chang et al.20,21) have demonstrated that the addition of Ag offers better solder joint reliability and hinders the formation of Kirkendall voids. However, only a few thermal characteristics of the solder alloy have been studied. The objectives of this study are (1) to build a database of thermal characteristics for the Sn-9Zn-0.5Ag solder alloy and (2) to determine the IMCs formed at the Sn-9Zn-0.5Ag/Cu interface after soldering.

2. Experimental Procedure

The compositions of the solder alloys used in this study were Sn-37Pb, Sn-3.5Ag (commercial grade, 99.9 mass% in purity). The Sn-9Zn and Sn-9Zn-0.5Ag solder alloys (in mass%) were melted with pure Sn, Zn and Ag metals (99.9 mass%). The pure metals were weighed and pickled in a 5 vol% HCl solution to remove oxides on the surface. Then they were mixed and melted at 600°C in a stainless steel crucible with stirring to homogenize. The molten solder alloys were cast into a 3 mm diameter cylinder and the microstructures of the solder alloys were observed with an optical microscope.

A differential scanning calorimeter (DSC, Universal V2.6D TA Instruments) was used to estimate the melting points of the solder alloys with In metal as a base material. The ramping rate was 3°C/min and the data was recorded from 100 to 270°C. Pure Sn was utilized as a standard to estimate the calibration coefficient K of the instrument. The area under the peak was integrated with a commercially available software to calculate the fusion heat of the solder alloys.

An oxygen-free and high conductivity (OFHC) Cu substrate of 60 mm × 25 mm × 0.5 mm was pickled in a 5 vol% HCl solution for 15 and then rinsed in de-ionized water for 10 s. After rinsing, the Cu substrate was degreased in a 5 mass% NaOH solution for 15 s at 70°C, rinsed in de-ionized water for 10 s again and finally immersed in a flux of
3.5 mass% dimethylammonium chloride (DMAHCl) to avoid reoxidation.

After fluxing, the Cu substrate was held in a dipping furnace as shown in Fig. 1. The dipping temperature was 250°C and the dipping times were 10, 20 and 30 s, respectively, at a dipping rate of 11.8 mm/s.

The unreacted solder alloy on the dipped sample was removed with sandpaper and an etching solution. An X-ray diffractometer (XRD, D-MAX III B, Rigaku, Japan) tool was employed to identify the phases in bulk solder and the IMCs formed at the Sn-9Zn-0.5Ag/Cu interface at a scanning rate of 1°/min for 2θ from 20 to 80° and Si powders as a standard for calibration.

The dipped sample was stuck together with epoxy, then ground and polished with sandpaper and 0.3 μm Al₂O₃ powder paste. Afterwards, it was etched with an etchant (2 vol% HCl + 3 vol% HNO₃ + 95 vol% C₂H₅OH). A scanning electron microscope (SEM, JXA-840, JEOL, Japan) was used to observe the morphology of the Sn-9Zn-0.5Ag/Cu interface, and energy dispersive spectrometer (EDS, AN10000/85S, LINKS, England) was utilized to determine the chemical compositions of the IMCs.

The dipped sample was sealed in a 3 mm Cu tube with G1 epoxy and baked at 120°C for 1 h to harden the epoxy. After baking, the sample was cross-sectioned and ground to a thickness below 100 μm, then thinned by using an ion-miller. A transmission electron microscope (TEM, HF-2000, HITACHI, Japan) with EDS (Voyager 1000, Noran) was utilized to determine the structure of the IMCs.

3. Structure and morphology of the IMCs formed at the Sn-9Zn-0.5Ag/Cu interface

Figures 2(a)–(d) show the DSC curves of the various solder alloys used in this study. It indicates that the melting points \( T_{\text{onset}} \) of the Sn-37Pb, Sn-9Zn, and Sn-3.5Ag eutectic alloys are 179.5, 195.5 and 220.4°C respectively, which are very close to the previous published results.\(^{16,22}\) When 0.5 mass% Ag is added to the Sn-9Zn solder alloy, the \( T_{\text{onset}} \) of the solder alloy increases from 195.5 to 196.7°C and the increment of 1.2°C is acceptable. Only one endothermic peak is found in the DSC curve, showing that the chemical composition of the Sn-9Zn-0.5Ag solder alloy is near eutectic.

The melting ranges \( (T_{\text{end}} - T_{\text{onset}}) \) of the Sn-37Pb, Sn-9Zn, Sn-9Zn-0.5Ag and Sn-3.5Ag solder alloys are 11.5, 12.6, 11.3 and 7.4°C, respectively. A narrow melting range can avoid the occurrence of segregation and hot tear in materials as reported by Vianco and Rejent.\(^{23}\) Hence, the Sn-3.5Ag solder alloy has excellent resistance to avoid segregation. The addition of Ag decreases the melting range of the Sn-9Zn solder alloy from 12.6 to 11.3°C, which is comparable to that of the Sn-37Pb solder alloy.

The heat of fusion, \( \Delta H \), is given by eq. (1):\(^{24}\)

\[
\Delta H = \frac{KA}{m}
\]

where K is the calibration coefficient depending on the shape of a crucible and regarded as a constant in the DSC system,\(^{25}\) \( m \) is the mass of a sample, and \( A \) is the area under the curve peak. The heat of fusion of pure Sn is 60.6 J/g\(^{26}\) and the A/m value is 22.96 J/g as shown in Fig. 2(e). From eq. (1), the calibration coefficient K of the DSC instrument is obtained as 2.64.

The DSC result of the various solder alloys shows that the heats of fusion, \( \Delta H_f \), for the Sn-37Pb, Sn-9Zn, and Sn-3.5Ag solder alloys are 104.2, 163.9 and 151.0 J/g, respectively, showing that the Sn-37Pb solder alloy needs the lowest energy for melting. Chen et al.\(^{10}\) have demonstrated that the Sn-37Pb solder alloy melts at 183°C and the enthalpy of fusion is 45.21 J/g. The melting point of the solder alloy reported by Chen et al.\(^{10}\) is close to our result, but the fusion heat is only one half of ours, because the K value of the DSC instrument has not been calibrated in the former study.

When 0.5 mass% Ag is added to the Sn-9Zn solder alloy, the heat of fusion of the solder alloy decreases dramatically from 163.9 to 74.7 J/g, showing that the Ag addition is beneficial to decrease the heat of fusion of the Sn-9Zn solder alloy. The heat of fusion of the Sn-9Zn-0.5Ag solder alloy is even lower than those of the Sn-37Pb and Sn-3.5Ag solder alloys and is a useful material for saving energy.

The XRD patterns of the Sn-9Zn and Sn-9Zn-0.5Ag bulk solders are shown in Figs. 3(a) and (b), in which the Sn-9Zn solder alloy is composed of Sn-rich and Zn-rich phase. However, the Zn-rich phase disappears in the bulk solder of Sn-9Zn-0.5Ag, showing that the Ag addition promotes the dissolution of Zn in Sn. Because Zn has a higher heat of fusion of 115.79 J/g and the heat of fusion for melting the Zn-rich phase in the Sn-9Zn solder alloy is not necessary to consume for the one of Sn-9Zn-0.5Ag, which make the Sn-9Zn-0.5Ag solder alloy have a heat of fusion close to pure Sn.

3.2 Structure and morphology of the IMCs formed at the Sn-9Zn-0.5Ag/Cu interface

Figures 4(a) and (b) are the XRD patterns of the Sn-9Zn/Cu and Sn-Zn-0.5Ag/Cu interfaces, showing that the η-Cu₆Sn₁₀ and η₁-Cu₂Zn₈ are formed at the Sn-9Zn/Cu interface. Yu et al.\(^{27}\) have reported the same result and that the
structures of the $\eta$-Cu$_6$Sn$_5$ and Cu$_5$Zn$_8$ are hexagonal and body centered cubic (bcc), respectively. Besides the $\eta$-Cu$_6$Sn$_5$ and Cu$_5$Zn$_8$, the monoclinic $\eta'$-Cu$_5$Sn$_3$ is also found at the Sn-9Zn-0.5Ag/Cu interface, showing that the Cu$_6$Sn$_5$ layer has two different structures. In the previous studies,$^{28,29}$ it was found that the IMCs formed at the Cu-Sn diffusion couple and Sn-37Pb/Cu interface are $\eta$-Cu$_6$Sn$_5$ and $\varepsilon$-Cu$_3$Sn. Suganuma et al.$^{30}$ have reported that the first IMC layer at the Sn-9Zn/Cu interface is Cu$_5$Zn$_8$. The IMC layers formed at the Sn-Zn-Al/Cu interface are Cu$_5$Zn$_8$ and Cu$_9$Al$_4$ as
reported by Yu et al.\textsuperscript{31} In the present study, the bi-structural Cu\textsubscript{6}Sn\textsubscript{5} and bcc Cu\textsubscript{5}Zn\textsubscript{8} layers coexist at the Sn-9Zn-0.5Ag/Cu interface, which are different from the result obtained in the Sn-9Zn solder system.\textsuperscript{30,31} It is caused by that Ag promotes the formation of the Cu\textsubscript{6}Sn\textsubscript{5} layer because Ag increases the solubility of Cu in Sn.\textsuperscript{32}

The Ag\textsubscript{3}Sn IMC forms at the solder alloy/Cu interface when the Ag content in solder alloy is above 0.1 mass% as reported by Huh et al.\textsuperscript{33} From the XRD pattern, the Ag\textsubscript{3}Sn is found at the Sn-9Zn-0.5Ag/Cu interface because the Ag content in the solder alloy is higher than 0.1 mass%.

The morphology of the Sn-9Zn-0.5Ag/Cu interface after dipping at 250°C for 10 s is shown in Fig. 5(a), which indicates that two different shaped IMCs layers are formed at the interface, namely, one is scalplo-shaped and the other is planar. The chemical composition of the scalplo-shaped IMC is determined as 51.9Cu-46.2Sn-1.2Zn-0.7Ag, showing that the IMC layer is Cu\textsubscript{6}Sn\textsubscript{5} and some Zn and Ag atoms dissolve in it. The planar IMC layer is determined as 42.8Cu-52.4Zn-4.4Sn-0.4Ag, showing that the IMC layer is Cu\textsubscript{5}Zn\textsubscript{8}.

Figures 5(b)–(e) show the mapping analysis of the Sn-9Zn-0.5Ag/Cu interface, indicating that Sn concentrates at the scalplo-shaped IMC layer, but Zn concentrates in the IMCs layers close to the Cu substrate, which agrees with the result of EDS analysis. Besides, Ag also concentrates in the scalplo-shaped Cu\textsubscript{6}Sn\textsubscript{5} layer. The effect of Ag dissolution on the formation of bi-structural Cu\textsubscript{6}Sn\textsubscript{5} is delineated as follows. From the thermodynamic data listed in Table 2, the Gibbs free energies of the Cu\textsubscript{5}Zn\textsubscript{8} and Cu\textsubscript{6}Sn\textsubscript{5} are lower than those of the Ag\textsubscript{3}Sn and Ag\textsubscript{4}Sn. Therefore, the Cu\textsubscript{5}Zn\textsubscript{8} and Cu\textsubscript{6}Sn\textsubscript{5} layers tend to be formed at the Sn-9Zn-0.5Ag/Cu interface. Yu et al.\textsuperscript{31} have also reported the similar result.

3.3 Structures of the IMCs at the Sn-9Zn-0.5Ag/Cu interface

Figures 6(a) and (b) show the bright field (BF) and dark field (DF) images of the IMCs at the Sn-9Zn-0.5Ag/Cu interface, indicating that the Cu\textsubscript{6}Sn\textsubscript{5} layer is formed at the interface close to the solder alloy and the Cu\textsubscript{5}Zn\textsubscript{8} layer is adjacent to the Cu\textsubscript{6}Sn\textsubscript{5} layer. The result agrees with the SEM micrograph. The Cu-Sn IMC has been determined as a monoclinic $\eta$-Cu\textsubscript{6}Sn\textsubscript{5} in our previous study.\textsuperscript{20} Figure 6(c) shows the EDS analysis of the $\eta$-Cu\textsubscript{6}Sn\textsubscript{5}, indicating that the dissolutions of Ag and Zn in the $\eta$-Cu\textsubscript{6}Sn\textsubscript{5} are 3.15 and 6.36 mass%, respectively. However, the Cu\textsubscript{6}Sn\textsubscript{5} layers with 0.33 mass% Ag and 0.80 mass% Zn are also found in the Cu-Sn IMC as shown in Fig. 6(d). The ED pattern of the Cu-Sn
IMC with lower Ag and Zn contents is shown in Fig. 6(e), showing that it is a hexagonal $\gamma$-Cu$_6$Sn$_5$ with zone axis (ZA) of $[1103]$. Westgren and Phrahmen$^{37}$ have reported that the Cu$_6$Sn$_5$ transforms from $\gamma$-Cu$_6$Sn$_5$ to $\gamma'$-Cu$_6$Sn$_5$ at a temperature around 170°C, where $\gamma$ is a high temperature phase with an ordered NiAs structure (hexagonal) and the $\gamma'$-Cu$_6$Sn$_5$ is a low temperature phase of a long periodic superlattice of $\eta$-Cu$_6$Sn$_5$ with a period of about 5 along both a and c directions.$^{38}$ Gangulee et al.$^{39}$ have demonstrated that quenching from about 170°C produc-

<table>
<thead>
<tr>
<th>Solders</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-37Pb</td>
<td>179.5</td>
<td>104.2</td>
<td>eutectic</td>
</tr>
<tr>
<td>Sn-3.5Ag</td>
<td>220.4</td>
<td>151.0</td>
<td>eutectic</td>
</tr>
<tr>
<td>Sn-9Zn</td>
<td>195.5</td>
<td>163.9</td>
<td>eutectic</td>
</tr>
<tr>
<td>Sn-Zn-0.5Ag</td>
<td>196.7</td>
<td>74.7</td>
<td>near-eutectic</td>
</tr>
<tr>
<td>Sn</td>
<td>229.5</td>
<td>60.6</td>
<td>pure metal</td>
</tr>
</tbody>
</table>

Table 1 DSC analysis for various solder alloys.

<table>
<thead>
<tr>
<th>Intermetallic compounds</th>
<th>$X_{Cu}$</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol)</th>
<th>$\Delta G$ calculated at 250°C (kJ/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Cu$_6$Zn$_5$</td>
<td>0.4</td>
<td>$-11.14$</td>
<td>1.62</td>
<td>$-12.26$</td>
<td>35)</td>
</tr>
<tr>
<td>$\eta$-Cu$_6$Sn$_5$</td>
<td>0.6</td>
<td>$-2.99$</td>
<td>7.73</td>
<td>$-7.03$</td>
<td>34)</td>
</tr>
<tr>
<td>$\eta'$-Cu$_6$Sn$_5$</td>
<td>0.5</td>
<td>$-1.99$</td>
<td>8.05</td>
<td>$-6.20$</td>
<td>34)</td>
</tr>
<tr>
<td>Ag$_2$Sn</td>
<td>0.7</td>
<td>$-2.68$</td>
<td>4.89</td>
<td>$-5.24$</td>
<td>36)</td>
</tr>
<tr>
<td>Ag$_2$Sn</td>
<td>0.8</td>
<td>$-3.20$</td>
<td>3.34</td>
<td>$-4.95$</td>
<td>36)</td>
</tr>
</tbody>
</table>

Table 2 Thermodynamic data of intermetallic compounds.

Fig. 5 (a) SEM micrograph of the Sn-9Zn-0.5Ag/Cu interface after dipping at 250°C for 10 s, and mapping analyses of (b) Ag, (c) Zn, (d) Sn and (e) Cu.
es an ordered NiAs structure, whereas slow cooling to room temperature shows extra superlattice spots. However, Larsson et al. have explicated that the \( \eta' \)-Cu\(_6\)Sn\(_5\) has a monoclinic structure and is a new superstructure type belonging to the NiAs-Ni\(_2\)In structure group.

In our previous study, the structure of the \( \eta' \)-Cu\(_6\)Sn\(_5\) was found agreeing with the observation of Larsson et al.\(^{40}\) But it is found that the Cu\(_6\)Sn\(_5\) layer is bi-structural, namely, \( \eta \) and \( \eta' \) phases coexisting at the Sn-9Zn-0.5Ag/Cu interface. The Ag atoms do not dissolve in the \( \eta' \)-Cu\(_6\)Sn\(_5\) at the Sn-3.5Ag/Cu interface even after aging at 170°C for 4 days as reported by Vianco et al.\(^{41}\) Suganuma and Nakamura have determined the Cu\(_6\)Sn\(_5\) layer formed at the Sn-3.5Ag/Cu interface after aging being the \( \eta \) phase not the \( \eta' \) one.\(^{42}\) Hence, the formation of the \( \eta' \)-Cu\(_6\)Sn\(_5\) is caused by the dissolution of Ag and Zn in the \( \eta \)-Cu\(_6\)Sn\(_5\), and it expands the lattice of the \( \eta \)-Cu\(_6\)Sn\(_5\).

The BF and DF images of the Ag\(_3\)Sn IMC formed at the Sn-9Zn-0.5Ag/Cu interface are shown in Figs. 7(a) and (b), indicating that the Ag\(_3\)Sn particles form at the Cu\(_5\)Zn\(_8\)/Cu interface, not in the solder matrix for the Sn-3.5Ag/Cu system as reported by Vianco et al.\(^{41}\) Figs. 7(c) and (d) are the ED patterns of the Ag\(_3\)Sn with the ZA of [011] and [111], respectively, showing that the Ag\(_3\)Sn has an orthorhombic
4. Conclusions

The results are summarized as follows:

(1) The composition of the solder can be kept near-eutectic when 0.5 mass% of Ag is added to the Sn-9Zn solder alloy. The near-eutectic temperature is 196.7°C and the solidification range of the solder alloy is even lower than the Pb-Sn alloy. The sequence of the fusion heats for the various solders are: Sn-9Zn > Sn-3.5Ag > Sn-37Pb > Sn-Zn-0.5Ag.

(2) The planar Cu₅Zn₈ and scallop-shaped Cu₆Sn₅ are found at the Sn-9Zn-0.5Ag/Cu interface. The Cu₆Sn₅ layer has two different structures, namely, η and η′ phases. Besides the Cu₅Zn₈ and Cu₆Sn₅, the Ag₃Sn particles with an orthorhombic structure are also found at the Sn-9Zn-0.5Ag/Cu interface close to the Cu substrate.

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