Synthesis of the Combination Solder of 80Au-20Sn/42Sn-58Bi and Thermodynamic Interpretation of the Microstructural Evolution

Chang Joon Yang, Moon Gi Cho and Hyuck Mo Lee*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Yusung-Gu, Daejeon, Republic of Korea 305-701

1. Introduction

In soldering electronic interconnections, we need to carefully design soldering processes such as the chip-to-module process and the module-to-board process. These soldering processes are called step soldering because the soldering is performed step by step. Module-to-board soldering requires a solder alloy that has a lower melting temperature ($T_m$) than the solder alloy used in the earlier step of chip-to-module soldering. The use of high-melting alloys in chip-to-module soldering provides a hierarchy of soldering temperatures, which ensures that the high-melting solders do not melt during the next level of module-to-board assembly with low-melting solders.

Traditionally, 37Pb-63Sn alloys ($T_m$, 183°C) have been used as a solder alloy for module-to-board soldering, whereas 97Pb-3Sn alloys ($T_m$, 310°C) have been used for chip-to-module soldering, and, the combination structure of 97Pb-3Sn/37Pb-63Sn, which comprised a high-melting solder alloy surrounded by a low-melting solder alloy, was suggested and used for the purpose of applying high-melting solder alloys to an organic substrate instead of a ceramic substrate.\(^1\) In addition, the combination structure was not influenced by next level assembly, because its remelting temperature increased. We also made a combination solder bump in a flip chip assembly by wrapping a 97Pb-3Sn solder bump on a chip with eutectic 37Pb-63Sn solder, after which the electromigration behavior was investigated.\(^2\)

Recently, Pb-free solder alloys have been extensively researched. The near-ternary eutectic Sn-Ag-Cu alloy is becoming a consensus candidate for 37Pb-36Sn alloys.\(^3,4\) However, there is scant research on Pb-free solder alloys that can replace the high-melting 97Pb-3Sn alloys. One strong candidate is the eutectic 80Au-20Sn solder alloy by weight (71Au-29Sn by molar content).\(^5,6\) By the way, Kim and Lee found that a layer consisted of Bi-rich matrix and small dispersed Au-Sn IMCs was formed by the interfacial reaction between Sn-58Bi and Au.\(^8\) Interestingly, remelting temperature of the layer was 220°C to 225°C, which was higher than that of a 42Sn-58Bi solder (138°C).\(^8\) In this study, the 80Au-20Sn/42Sn-58Bi combination solder is suggested as an alternative to the 97Pb-3Sn/37Pb-63Sn combination structure. In this combination structure, 97Pb-3Sn is substituted by 80Au-20Sn and 37Pb-63Sn is replaced by 42Sn-58Bi that has a much lower melting temperature of 138°C. By using an 80Au-20Sn/42Sn-58Bi combination structure that can be applied to organic substrates, we investigate and thermodynamically analyze the microstructures of the combination solder and the intermetallic compounds (IMCs) which formed in the solder joints of 80Au-20Sn/42Sn-58Bi. Finally, the microstructural change inside 42Sn-58Bi solder of the combination structure is also discussed.

2. Experimental Procedures

After preparing the solder alloys from elements with purity higher than 99.99%, we encapsulated the solder alloys under vacuum in quartz tubes and melted and mixed the alloys perfectly. Then, as-cast 80Au-20Sn alloys were fabricated into ball shapes with a diameter of 650 μm using a laboratory-based ball manufacturing apparatus. A commercial solder paste of 42Sn-58Bi solder alloys was used, and, two types of screen-printing masks with different sized holes were used in order to control the volume of this paste. The substrate was a printed circuit board (PCB) with bond pads, which was also commercially fabricated. The pad was constructed as under bump metallization (UBM) of the solder joint.

Figure 1 is the fabrication process to make an 80Au-20Sn/42Sn-58Bi combination structure. First, to solder the 80Au-20Sn solder balls, we used the sessile drop method. An isothermal soldering was performed on a hot plate at 330°C for 90 s. Then, after screen-printing on a Cu/Ni/Au pad with a 42Sn-58Bi solder paste, we aligned the refloowed 80Au-20Sn solder with the screen-printed 42Sn-58Bi solder. An
additional reflow was conducted on a hot plate at 200°C for 120 s with an RA-type flux in order to build up the combination structure.

Each solder joint was etched in a solution of methanol, nitric acid and hydrochloric acid. We then used the back-scattered electron mode of scanning electron microscopy (SEM) to investigate the IMCs, and energy-dispersive X-ray spectroscopy (EDS) for the compositional analysis. Moreover, for all the thermochemical calculations, we used the Thermo-Calc thermochemical software developed at the Royal Institute of Technology, Stockholm, Sweden. 9)

3. Results and Discussion

3.1 Observation of microstructures and IMCs

Figure 2(a) shows a cross-sectioned image of the 80Au-20Sn/42Sn-58Bi combination structure. The 80Au-20Sn solder was successfully wrapped in a large volume of 42Sn-58Bi solder. We divided the IMC phases observed in Fig. 2(a) into four parts: at the interface of Au-Sn with Cu/Ni/Au UBM (Fig. 2(b)), at the interface between Au-Sn and Sn-Bi (Figs. 2(c) and 2(d)), inside the Sn-Bi solder (Fig. 2(e)) and, finally, at the interface of Sn-Bi with Cu/Ni/Au (Fig. 2(f)). We then used EDS to analyze the four parts, the results of which are shown in Table 1.

Figure 2(b) shows that an IMC phase comprising 40.02 ± 0.83 at% Sn, 32.48 ± 0.62 at% Ni and 27.5 ± 2.19 at% Au was observed at the interface between the Au-Sn solder and the Cu/Ni/Au UBM. By using an atomic ratio, we identified the interfacial IMC phase as $(\text{Au},\text{Ni})_3\text{Sn}_2$ with the substitution of Au atoms on the Ni sites. This result is consistent with the work of Kim et al., who reported that $(\text{Au},\text{Ni})_3\text{Sn}_2$ formed during the interfacial reaction of Au-Sn and an Ni substrate. 5)

The Au-Sn solder, which typically has a lamellar microstructure, is composed of AuSn (β phase) and Au$_5$Sn (γ phase). The bright constituent in the eutectic microstructure is the γ phase, whereas the darker constituent is the β phase. The large islands of the γ phase in Fig. 2(b) seem to have been caused by the Au that dissolved from the thin protective Au layer in the UBM, which we deposited to ensure the wetting of the solder. Once the solder became molten, the Au layer dissolved and slightly increased the Au content in the liquid solder. This process caused the Au-Sn solder to have an off-eutectic composition, and it enabled the proeutectic formation of the γ phase. Our results are consistent with the findings of Kim et al. 5) and Song et al., 7) with the only difference being that Song et al. 7) used a different UBM structure of Cu/electroless Ni-P/Au.

The Au-Sn solder, which typically has a lamellar microstructure, is composed of AuSn (β phase) and Au$_5$Sn (γ phase). The bright constituent in the eutectic microstructure is the γ phase, whereas the darker constituent is the β phase. The large islands of the γ phase in Fig. 2(b) seem to have been caused by the Au that dissolved from the thin protective Au layer in the UBM, which we deposited to ensure the wetting of the solder. Once the solder became molten, the Au layer dissolved and slightly increased the Au content in the liquid solder. This process caused the Au-Sn solder to have an off-eutectic composition, and it enabled the proeutectic formation of the γ phase. Our results are consistent with the findings of Kim et al. 5) and Song et al., 7) with the only difference being that Song et al. 7) used a different UBM structure of Cu/electroless Ni-P/Au.

Figure 2(c) shows the two types of IMC layers that we observed at the combination interface of the Au-Sn solder and the Sn-Bi solder. In addition, the EDS analysis in Table 1 shows that the IMC layer (with the lighter contrast) near the
Au-Sn side consisted of 48 at% of Au and 52 at% of Sn, which was identified as AuSn. In contrast, the IMC layer (with the darker contrast) near the Sn-Bi side consisted of 32 at% to 34 at% Au and 66 at% to 68 at% Sn, which was identified as AuSn. In the Sn-rich phase (the dark constituent) and the Bi-rich phase (the light constituent) of the Sn-Bi matrix, a typical eutectic structure was observed, as seen in Fig. 2(d). A rod-type IMC was also found in the solder matrix, which was identified as AuSn. When we etched away the Sn-Bi solder matrix, as shown in Fig. 2(e), the AuSn2 IMCs had a plate-type appearance. The large plate-type AuSn2 IMC would be resulted from the neighboring Au-Sn solder through diffusion.

Finally, as shown in Fig. 2(f), the IMC phase that consisted of 57 at% Sn, 31 at% to 40 at% Ni and 3 at% to 12 at% Au was observed directly at the interface of the Sn-Bi solder and the Ni/Au UBM. By using an atomic ratio, we identified the IMC phase as (Au,Ni)2Sn4 with the substitution of Au atoms on the Ni sites. We also observed another IMC layer with a relatively light contrast above the (Au,Ni)2Sn4 layer. This layer was identified as AuSn: AuSn4: AuSn4, (Au,Ni)2Sn4 and β-Sn (body-centered tetragonal). Hence, (Au,Ni)2Sn4 and AuSn4 form at the joint interface and this formation, as shown in Fig. 2(f), is also in good agreement with our experimental observation. Moreover, our EDS measurements show that the Au content in the (Au,Ni)2Sn4 is about 3 at% to 12 at%.

3.2 Thermodynamic analysis

The phase diagram of the related system was used in order to explain the interfacial reactions between the solders and the UBM. Figures 3(a), 3(b) and 3(c) show isothermal phase diagrams of a ternary Sn-Ni-Au system at 330°C, 200°C and room temperature, respectively, which were calculated with the thermodynamically assessed parameters in Ref. 12). The compositions are shown in atomic percentage rather than weight percentage. When the eutectic Au-Sn solder (which has a molar content of 71Au-29Sn) reacted with Ni/Au UBM at 330°C, the contribution of the Au UBM (0.1 μm) can be neglected because it is deposited more thinly than the Ni UBM (3 μm). The line inserted in Fig. 3(a) connects the compositions of 71Au-29Sn and Ni UBM, and represents their interfacial reactions during reflow. The straight line passes through a ternary equilibrium region of the liquid, Ni3Sn2 and hcp, and the liquid phase is in equilibrium with Ni3Sn2, as shown in Fig 3(a). When the eutectic Au-Sn solder is in contact with the Ni UBM as in Fig. 2(b), the eutectic phases (AuSn and Au4Sn) are in equilibrium with (Au,Ni)2Sn3 at room temperature. It is also consistent with the isothermal phase diagrams of a ternary Sn-Ni-Au at room temperature, as shown in Fig. 3(c). As a result, we expected, from a thermodynamic point of view and in line with our experimental observations, that the (Au,Ni)2Sn3 IMC phase would form at the interface of the Au-Sn and the UBM.

The IMC phases of (Au,Ni)2Sn4 and AuSn4 formed at the interface of the Sn-Bi solder and the Ni UBM. The same ternary phase diagram was also used to explain this formation because Bi atoms do not form intermetallic compounds with Sn and Ni, and the solubility of Bi in Sn and Ni is not large, and thus the quaternary system of interest in this work can be reduced to the ternary Sn-Ni-Au system. We can make an quantitative analysis of the interfacial reactions with isothermal phase diagrams at 200°C and room temperature in Figs. 3(b) and 3(c). The interface of the Sn-Bi solder and the Ni UBM is located in the Sn-rich corner that contains a slight amount of Ni and Au because Ni and Au can dissolve into the Sn-Bi solder. As shown in Figs. 3(b) and 3(c), this composition can be found inside a three-phase equilibrium region of AuSn4, (Au,Ni)2Sn4 and β-Sn (body-centered tetragonal), Hence, (Au,Ni)2Sn4 and AuSn4 form at the joint interface and this formation, as shown in Fig. 2(f), is also in good agreement with our experimental observation. Moreover, our EDS measurements show that the Au content in the (Au,Ni)2Sn4 is about 3 at% to 12 at%.

Neumann et al.\textsuperscript{11,12) reported the existence of a stable ternary compound, Sn4AuNi2, in the Sn-rich corner of the Sn-Ni-Au system at 400°C. In addition, they asserted that the stable ternary compound, Sn4AuNi2 was a separate one from any other compound in the Sn-Ni-Au system, including the (Au,Ni)2Sn4 phase which contains a negligible amount of Au.\textsuperscript{12) Subsequently, Liu et al.\textsuperscript{10) conducted experimental measurements of the ternary Sn-Ni-Au system and obtained the relevant ternary thermodynamic parameters to describe the system. In the Sn-rich corner at 200°C, Liu et al.\textsuperscript{10) obtained a three-phase equilibrium of Sn3AuNi3, (Sn8.57)Au0.143Ni0.8586, exactly), Ni3Sn4 (with Au content of only 0.003), and AuSn4. Our study, however, reveals that the

<table>
<thead>
<tr>
<th>location</th>
<th>Au (at%)</th>
<th>Ni (at%)</th>
<th>Sn (at%)</th>
<th>phase formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>interface between 80Au-20Sn solder and Cu/Ni/Au</td>
<td>27.5 (±2.19)</td>
<td>32.48 (±0.62)</td>
<td>40.02 (±0.83)</td>
<td>(Au,Ni)3Sn2</td>
</tr>
<tr>
<td>interface between 80Au-20Sn solder and Sn-58Bi solder</td>
<td>48.64 (±0.32)</td>
<td>51.36 (±0.94)</td>
<td>AuSn</td>
<td></td>
</tr>
<tr>
<td>inside the Sn-58Bi solder</td>
<td>32 ~ 34 (±0.5)</td>
<td>66 ~ 68 (±0.69)</td>
<td>AuSn2</td>
<td></td>
</tr>
<tr>
<td>interface between Sn-58Bi solder and Cu/Ni/Au</td>
<td>3.08 ~ 12.03 (±0.5)</td>
<td>26.86 ~ 39.33 (±0.20)</td>
<td>56.54 ~ 57.29 (±0.3)</td>
<td>(Au,Ni)2Sn4</td>
</tr>
</tbody>
</table>

Table 1 EDS compositions (in atomic percentage) of IMCs formed in the 80Au-20Sn/Sn-58Bi combination structure.
$\beta$-Sn phase is in contact with (Au,Ni)$_3$Sn$_4$ and AuSn$_4$. Hence, the main discrepancy in experimental studies lies in the solubility of the Au in (Au,Ni)$_3$Sn$_4$. In our study and in the work of Anhock et al., the Au solubility ranges from 3 at% to 12 at%.

The phase diagram of the ternary Sn-Au-Bi system, which is shown in Figs. 4(a) and 4(b), helps us to understand the interfacial reaction at the interface of the Au-Sn solder and the Sn-Bi solder. The thermodynamically assessed parameters in the binary systems of Sn-Au, Au-Bi and Bi-Sn...
Equation as followed: calculate the volume of Sn-Bi solder geometrically with the expressing the results in several equations. We can also calculating the volume of a lower eutectic 37Pb-63Sn solder and made a good combination structure by geometrically calculating the volume of the Sn-58Bi solder paste. Powell and Trivedi\textsuperscript{17}) were used to calculate the isothermal phase diagrams of Sn-Au-Bi. The ternary interaction parameters were not used due to lack of reliable data. Figure 4(a) shows an isothermal phase diagram of the ternary Sn-Au-Bi system calculated at 200°C. The line inserted in Fig. 4(a) connects the compositions of 71Au-29Sn and 57Sn-43Bi (by molar content), and the arrow represents the mass balance line. The Sn-Bi solder is liquid but the Au-Sn solder is solid during a reflow at 200°C. Furthermore, the Sn-Bi solder is in equilibrium with AuSn\textsubscript{2} as soon as the Au atoms are diffused into the liquid Sn-Bi solder. Upon further reaction, the AuSn phase shows up in addition to AuSn\textsubscript{2}. This result is in good agreement with the finding of Fig. 2(c). The interface was composed of AuSn\textsubscript{2} on the side of the Sn-Bi solder and AuSn on the side of the Au-Sn solder.

At room temperature, the liquid phase became solid. Figure 4(b) shows an isothermal phase diagram of the same Sn-Au-Bi system calculated at room temperature. By now, the Sn-Bi solder contains some Au (through diffusion from the Au-Sn solder) in the three-phase equilibrium region of \( \alpha \)-Sn, rhombohedral Bi and AuSn\textsubscript{2}. The existence of several large plate-type AuSn\textsubscript{2} particles, as shown in Figs. 2(d) and 2(e), confirms this expectation.

### 3.3 Volume control of an Sn-58Bi solder for the purpose of obtaining a combination structure

From the industrial viewpoint, the relative amounts of the Au-Sn solder and the Sn-Bi solder in Fig. 2(a) are unrealistic. Kim and Lee\textsuperscript{8}) observed the formation of a layer that consisted of a Bi-rich matrix and small dispersed Au-Sn particles from the interfacial reaction between Sn-58Bi and Au. The Au layer in their experimental setup was a thin film type. In our study and in the electronic packaging of interest, the thin film type is hard to implement. Hence, to obtain a successful combination structure, we must therefore control the volume of the Sn-58Bi solder paste. Powell and Trivedi\textsuperscript{17}) made a good combination structure by geometrically calculating the volume of a lower eutectic 37Pb-63Sn solder and expressing the results in several equations. We can also calculate the volume of Sn-Bi solder geometrically with the equation as followed:

\[
V = \frac{\pi h}{24} (3d_{\text{top}}^2 + 3d_{\text{bottom}}^2 + 4h^2)
\]

Where
\( V = \) The volume of a truncated sphere in the solder joint
\( h = \) Height of the solder joint
\( d_{\text{top}} = \) Top diameter of UBM (can = 0)
\( d_{\text{bottom}} = \) Bottom diameter of PCB pad (can = 0)

The diameters of the PCB pad, UBM and Au-Sn solder use in this study were 600 µm, 400 µm and 650 µm respectively. The height of the combination solder structure was also calculated by the same equation \( (d_{\text{bottom}} = 0) \). Then we could determine the optimum volume of the Sn-Bi solder to be \( 8.347 \times 10^{-11} \text{ m}^3 \) by subtracting the volume of the Au-Sn solder from the calculated volume \( (V) \). Note, however, that the volume of Sn-Bi solder used to obtain the combination solder structure in Fig. 2(a) was \( 1.248 \times 10^{-10} \text{ m}^3 \), which is slightly larger than the optimum volume.

In the study of Kim and Lee,\textsuperscript{16}) most of the Sn elements were consumed by a reaction with the Au elements, leading to the attainment of a Bi-rich matrix dispersed with Au-Sn particles. The resultant microstructure increased the remelting temperature to a range of 220°C to 225°C, which is beneficial in that the combination solder made in this way does not melt again in the next level of the assembly. Their works prompting us to significantly reduce the volume of the Sn-Bi solder to \( 2.058 \times 10^{-11} \text{ m}^3 \) as controlling the volume of the Sn-Bi paste by a screen-printing mask with different sized holes.

Figure 5(a) shows the final combination structure obtained in this way. Because of the small volume of Sn-Bi, the Sn-Bi solder cannot sufficiently envelope the Au-Sn solder. From Figs. 5(b) and 5(c), which show SEM micrographs of the microstructure inside the Sn-Bi solder, we can see that the microstructure of the Sn-Bi solder is coarser than the microstructures shown in Figs. 2(e) and 2(f). We also found AuSn\textsubscript{2} particles in the Sn-Bi solder. In addition, as shown in Fig. 5(c), the microstructures show more Bi-rich regions (light contrast). Nonetheless, large Sn-rich regions (dark contrast) are still present in the Bi-rich regions even though the volume of the Sn-Bi solder is significantly decreased. This phenomenon implies that the volume of Sn-Bi solder found under our experimental conditions is still too large to form microstructures of Sn-Bi solder that is composed solely of Bi-rich regions and dispersed Au-Sn particles, without Sn-rich regions. However, any further decrease in the volume of Sn-Bi solder prevents the formation of a good combination structure. We deduce, therefore, that there is a limit in the optimum solder volume for a well-defined combination solder structure that can be applied to organic substrates with an increased remelting temperature.

### 4. Summary

We fabricated a Pb-free combination solder of high-melting 80Au-20Sn completely wrapped in low-melting Sn-58Bi. The (Au,Ni)\textsubscript{3}Sn\textsubscript{2} phase was observed at the interface of

---

**Fig. 5** Cross-sectioned images of the 80Au-20Sn/Sn-58Bi combination structure with a small volume of Sn-58Bi solder: (a) overview and magnified images (b) inside Sn-58Bi solder and (c) near the interface of Sn-58Bi solder and Cu/Ni UBM.
the Au-Sn solder and the Ni/Au UBM, while the phases of (Au,Ni)$_3$Sn$_4$ and AuSn$_4$ were observed at the interface of the Sn-Bi solder and the Cu/Ni/Au UBM. The interfacial reaction between the Au-Sn solder and the Sn-Bi solder resulted in the formation of AuSn$_2$ on the side of the Sn-Bi solder and AuSn on the side of the Au-Sn solder. We explained all of these interfacial reactions by using relevant equilibrium phase diagrams.

In conclusion, we found that there is a limit in the optimum solder volume for a well-defined combination solder microstructure that can be applied to organic substrates with an increased remelting temperature.

Acknowledgments

This study was supported by a grant from the Center for Electronic Packaging Materials, which operates under aegis of the MOST and KOSEF (grant # R11-2000-085-08006-0).

REFERENCES