Effects of reflow and cooling conditions on interfacial reaction and IMC morphology of Sn–Cu/Ni solder joint
Jeong-Won Yoon, Sang-Won Kim, Seung-Boo Jung *
Department of Advanced Materials Engineering, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Suwon 440-746, South Korea
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Abstract
The interfacial reaction and morphology change of intermetallic compound (IMC) between eutectic Sn–Cu solder and Ni substrate under various reflow and cooling conditions were investigated. The reaction between the solder and Ni layer resulted in the formation of (Cu,Ni)6Sn5 IMC at the interface. Reflow and cooling conditions changed the morphology of the IMCs formed at the interface. At low temperatures (≤255°C), only a needle-type (Cu,Ni)6Sn5 IMC with a hexagonal cross-section was formed. On the other hand, the morphology of the (Cu,Ni)6Sn5 IMC changed from needle-type to dodecahedron-type with increasing reflow temperature and time. The morphology of the (Cu,Ni)6Sn5 IMC was also affected by cooling condition. Even though the morphology of the IMC changed with the reflow and cooling conditions, these IMCs had a similar chemical composition.

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Keywords: Sn–0.7Cu solder; Ball-grid-array (BGA); Interfacial reaction; Intermetallic compound (IMC); Lead (Pb)-free solder

1. Introduction
Pb-free solders have attracted much attention as substitution for the conventional Sn–Pb solders in order to cope with environmental issues [1,2]. Among several Pb-free candidate alloys, the eutectic Sn–0.7Cu (in wt.%) solder is one of the most promising Pb-free candidates to replace the Sn–Pb solders [3,4]. In addition to solder, printed circuit boards (PCBs) and component surface finishes also have to be Pb-free [3]. The Ni layer also is one of the most common surface finishes for the electronic packages. For solder joints, intermetallic compounds (IMCs) play an important role in bonding process between solder and substrate or UBM (under bump metallization). Many studies have been performed on the interfacial reaction and growth mechanism of IMCs between Sn–Pb or Pb-free solders and Ni layer during reflow and/or aging [1,3–7]. And, it is known that the formation of ternary Cu–Ni–Sn ((Cu,Ni)6Sn5) and/or (Ni,Cu)3Sn4 IMCs is the direct result of reaction between Cu-contained solders and Ni substrates [3,4].

Generally, reflow soldering is one of the key soldering approaches to produce solder joints. The temperature–time profile for the reflow has to be carefully chosen to produce reliable solder joints [8]. In addition, post-reflow cooling rate is also an important parameter. The cooling rate affects the microstructure of bulk solder and IMC layer at the interface, which in turn affects the reliability of the solder joint [7].

The main objective of this paper is to study the effects of reflow condition and post-reflow cooling rate on the morphology and growth of the ternary Cu–Ni–Sn IMC formed between Sn–0.7Cu solder and Ni substrate.

2. Experimental procedures
To investigate the interfacial reaction and microstructural evolution of the Sn–Cu solder/electrolytic Ni samples, reflow experiments were performed. The materials used in this study were commercially available ball-grid-array (BGA) solder
ball and substrate. The BGA solder ball was a eutectic Sn-0.7 wt.%Cu with a diameter of 500 μm. The substrate was a BT (Bismaleimide Triazine) laminate with bond pads whose nominal size and shape were defined through a circular opening of 460 μm diameter. The pad was constructed by electroplated Au/Ni over an underlying Cu pad. The thickness of the Au and Ni layers was 0.5 and 8.5 μm, respectively.

The solder balls were bonded to the BGA substrates in a reflow process employing rosin mildly activated (RMA) flux. The samples were then reflowed in the reflow machine (SAT-5100 + profile temperature raise heater, Rhesca Co., Japan) for different holding times from 1 to 60 s at four kinds of reflow temperatures 245, 255, 265 and 275 °C, respectively. The reflow times mean a duration time at peak temperature. And then, samples reflowed at 275 °C were cooled to room temperature in the reflow oven (slow cooling, about −1 °C/s) and in air (fast cooling, about −2 °C/s) to investigate the effect of cooling rate on the interfacial reaction and IMC morphology. These samples were prepared for observations on the cross-section as well as from the top of the IMC formed at the Sn–0.7Cu solder/Ni interface. The common metallographic practice was used to prepare the samples. An etchant of 95% CH₃OH–4% HNO₃–1% HCl was used to reveal the cross-sectional microstructure. Also, in order to observe the top view of the IMCs, majority of the solder on the specimens was first ground away. The ground specimens were then etched with 90% CH₃OH–10% HNO₃ to dissolve the remaining solder. The microstructures and chemical compositions were observed with a scanning electron microscopy (SEM, HITACHI S-3000H) equipped with energy dispersive X-ray (EDX). Also, the compositions of the phases formed at the interface were determined by a JEOL JXA-8900R (Tokyo, Japan) Electron Probe Micro Analyzer (EPMA) with wavelength dispersive X-ray (WDX).

3. Results and discussion

Fig. 1 shows the top view images of the IMC morphology for the Sn–0.7Cu/Ni joints reflowed under various reflow conditions. The reflowed-specimens were cooled to room temperature in the reflow machine. EPMA analysis confirmed that IMCs formed between solder and Ni were (Cu,Ni)₆Sn₅. These (Cu,Ni)₆Sn₅ IMCs were composed of 30.6–43.7 at.%Cu, 11.9–20.8 at.%Ni and 43.8–48.6 at.%Sn. From the top view micrographs, three types, namely needle-type IMC with a hexagonal cross-section (representatively Fig. 1(b)), cylinder-type IMC with a hexagonal cross-section and pointed tips (Fig. 1(d)), and dodecahedron-type IMC (Fig. 1(l)), of (Cu,Ni)₆Sn₅ morphology are observed in these Sn–Cu/Ni samples reflowed under different reflow conditions. In detail, at low reflow temperatures (≤255 °C), only a needle-type (Cu,Ni)₆Sn₅ IMC with a hexagonal cross-section was formed at the interface. When reflow time extended to 60 s, the size of these needle-type IMCs grew with reflow time, but there was no shape change. On the other hand, at higher reflow temperatures (≥265 °C), the morphology of the (Cu,Ni)₆Sn₅ IMC changed from needle-type to dodecahedron-type (or polyhedron-type) with increasing reflow temperatures and times. In other words, at reflow temperature of 265 °C, needle-type IMCs with hexagonal cross-section gradually changed into polyhedron-type IMCs.
Table 1: EPMA analysis results of IMCs formed at the Sn–0.7Cu/Ni interface, shown in Fig. 1.

<table>
<thead>
<tr>
<th>Analysis pointa</th>
<th>Cu (at.%)</th>
<th>Ni (at.%)</th>
<th>Sn (at.%)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.85</td>
<td>16.68</td>
<td>48.47</td>
<td>(Cu,Ni)6Sn5</td>
</tr>
<tr>
<td>2</td>
<td>39.22</td>
<td>16.96</td>
<td>43.82</td>
<td>(Cu,Ni)6Sn5</td>
</tr>
<tr>
<td>3</td>
<td>41.03</td>
<td>14.30</td>
<td>44.67</td>
<td>(Cu,Ni)6Sn5</td>
</tr>
<tr>
<td>4</td>
<td>43.72</td>
<td>11.89</td>
<td>44.39</td>
<td>(Cu,Ni)6Sn5</td>
</tr>
<tr>
<td>5</td>
<td>37.98</td>
<td>16.51</td>
<td>45.51</td>
<td>(Cu,Ni)6Sn5</td>
</tr>
<tr>
<td>6</td>
<td>30.57</td>
<td>20.82</td>
<td>48.61</td>
<td>(Cu,Ni)6Sn5</td>
</tr>
</tbody>
</table>

a Analysis points were indicated in Fig. 1.

with increasing reflow time. In addition, the polyhedron-type IMCs formed at the interface of the sample reflowed at 275 °C for 1 s grew abnormally into the dodecahedron-type IMCs with increasing reflow time, as shown in Fig. 1(d), (h) and (l). And, small dodecahedron-type (Cu,Ni)6Sn5 particles were in-between big dodecahedron-type (Cu,Ni)6Sn5 particles, as shown in Fig. 1(h) and (l). It was very interesting that the morphology of IMC changed with reflow conditions. Quantitative results of EPMA analyses for IMC phases formed at these interfaces are shown in Table 1. As shown in Table 1, these IMCs had a similar chemical composition.

Fig. 2 shows the cross-sectional SEM micrographs of the Sn-0.7Cu/Ni interfaces reflowed under various reflow conditions. During initial reflow, the topmost Au layer dissolved into the molten solder, leaving the Ni layer exposed to the molten Sn–Cu solder. The reaction between the molten solder and Ni layer resulted in the formation of commonly known (Cu,Ni)6Sn5 IMC at the interface. In the Sn-0.7Cu solder, the reaction of Cu and Sn is so important that it determines the formation of (Cu,Ni)6Sn5 IMC even though the Cu content in the solder is very low (0.7 wt.%) [3,4]. In this study, the result on the interfacial structure from cross-sectional SEM micrographs of Fig. 2 is consistent well with that of top view images shown in Fig. 1. As mentioned above, at reflow temperatures below 255 °C, only a needle-type (Cu,Ni)6Sn5 IMC was formed at the interface. Also, as shown in Fig. 2(h), small dodecahedron-type (Cu,Ni)6Sn5 particles were in-between (or underneath) big dodecahedron-type (Cu,Ni)6Sn5 particles in the sample reflowed at 275 °C for 60 s, as will be represented later. Furthermore, many voids (indicated by white arrows in Fig. 2(g) and (h)) existed between these (Cu,Ni)6Sn5 IMC particles. These voids were originally trapped solder. During sample preparation, the trapped solder in these voids was etched away. Compared to Fig. 2(d), (g) and (h), it was known that the upper big dodecahedron-type (Cu,Ni)6Sn5 IMC grew abnormally with increasing reflow temperature and time.

Fig. 3(a) and (b) shows the results of EPMA line analyses of the Sn-0.7Cu/Ni interfaces reflowed at 245 and 275 °C for 1 s, respectively. These EPMA analysis results clearly showed the existence of only (Cu,Ni)6Sn5 layer at the interface. As reflow temperature increased, a thicker (Cu,Ni)6Sn5 IMC layer formed at the interface. On the other hand, the thickness of the Ni layer decreased.

Fig. 4(a) shows the enlarged SEM micrograph of the Sn-0.7Cu/Ni interface reflowed at 275 °C for 60 s. As mentioned before, small (Cu,Ni)6Sn5 IMC particles were in-between big (Cu,Ni)6Sn5 IMC particles and these two IMCs had a same composition. Fig. 4(b) shows the result of EPMA line profile at the interface. The EPMA line analysis was performed along the white line of Fig. 4(a).

Fig. 5(a) and (b) shows the top views of IMCs formed at the Sn-0.7Cu/Ni interface cooled with two different cooling rates after reflowing at 275 °C for 1 s. As shown in Fig. 5, the morphology of (Cu,Ni)6Sn5 IMC changed under different cooling rates. When the cooling rate was fast, the (Cu,Ni)6Sn5 IMC was almost needle-type with a hexagonal cross-section (see Fig. 5(b)). On the other hand, when the cooling rate was slow, the size of the (Cu,Ni)6Sn5 IMC became lager, and cylinder-type IMCs with a hexagonal cross-section and pointed tips formed at the interface (see Fig. 5(a)). In addition, top view SEM micrographs of (Cu,Ni)6Sn5 IMCs formed at the Sn-0.7Cu/Ni interface cooled with two different cooling...
Fig. 3. EPMA line profiles of the Sn–0.7Cu/Ni interfaces reflowed at (a) 245 °C and (b) 275 °C for 1 s.

Fig. 4. (a) Enlarged SEM micrograph of the Sn–0.7Cu/Ni interface reflowed at 275 °C for 60 s and (b) EPMA line profile result along the white line of (a).

Fig. 5. Top view SEM micrographs of the Sn–0.7CuNi interface reflowed under different reflow times and cooling conditions.
rates after reflowing at 275 °C for 60 s are shown in Fig. 5(c) and (d). When cooling rate was fast, cylinder-type IMCs with a hexagonal cross-section and pointed tips formed at the interface, as shown in Fig. 5(d). On the other hand, when cooling rate was slow, dodecahedron-type (Cu,Ni)6Sn5 IMCs were observed. According to these results, the formation of the dodecahedron-type (Cu,Ni)6Sn5 IMC was sensitively affected by cooling rates during solidification. In other words, a cooling rate affected the formation and morphology of IMC in the cooling stage of reflow process. It was interesting that the IMC morphology changed with post-reflow cooling condition. Generally, a fast cooling rate results in an easier nucleation. But, in that case, since the holding time at high temperature is shorter, the effective time for IMC growth is shorter. This results in the formation of fine needle-type IMCs. When a cooling rate is slow, a nucleation rate is lower but IMC grains have enough time to grow. As a result, dodecahedron-type IMCs become dominant. Fig. 6 shows the cross-sectional SEM micrographs corresponding to Fig. 5. The result on the interfacial structure from these cross-sectional SEM micrographs was consistent with that of top view images shown in Fig. 5.

Fig. 7 shows the schematic diagram of the IMC morphological transition with reflow temperature, time and/or cooling rate used in this study. With increasing reflow temperature and/or time, the initial needle-type IMC changed

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**Fig. 6.** SEM micrographs of the Sn-0.7Cu/Ni interface reflowed under different reflow times and cooling conditions.

**Fig. 7.** Schematic diagram of the IMC morphological transition.
into the cylinder-type IMC with a hexagonal cross-section and pointed tips, and then turned into the dodecahedron-type IMC. In other words, the needle-type IMC with a hexagonal cross-section would have a preferred growth orientation, that is, a \( \langle 0001 \rangle \) orientation of hexagonal structure. As a result, tips of the hexagonal prism turned into pointed tips. And then, these IMCs grew along the orientation of hexagonal prism planes. In result, dodecahedron-type IMCs were formed. The formation of the polyhedron-type (the cylinder-type IMC with a hexagonal cross-section and pointed tips in this study) and/or dodecahedron-type IMCs resulted from an anisotropy of the interface energy of the \((\text{Cu,Ni})_6\text{Sn}_5\) phase \[9,10\]. Generally, the slowest-growing crystallographic planes always dictate the growth habit of the crystal. In other words, the anisotropy of the interface energy lead to a characteristic crystal form, which is bounded by the slowest growing faces \[10\].

In conclusion, IMCs with different morphologies formed at the Sn–0.7Cu/Ni interface when the reflow and cooling conditions changed. The interfacial reactions (the thickness and morphology of the IMC) correlate to the shear strength of the solder joint as well as its electrical resistance \[11\]. The investigation of the effect of IMC morphology on the shear strength of the solder joint is ongoing. The results of this study imply that the conditions of reflow and cooling must be strictly controlled to produce the desired IMC layer at the interface.

4. Conclusions

In this study, the interfacial reaction and morphology change of IMC between eutectic Sn–Cu solder and Au/Ni electroplated Cu substrate under various reflow and cooling conditions were investigated. The reaction between the solder and Ni layer resulted in the formation of well-known \((\text{Cu,Ni})_6\text{Sn}_5\) IMC at the interface. The reflow condition changed the morphology of the IMCs formed at the interface. At low temperatures (\(<255 \, ^\circ C\)), the needle-type \((\text{Cu,Ni})_6\text{Sn}_5\) IMC with a hexagonal cross-section was formed. On the other hand, the morphology of the \((\text{Cu,Ni})_6\text{Sn}_5\) IMC changed from needle-type to dodecahedron-type with increasing reflow temperature and time. Furthermore, the morphology of the \((\text{Cu,Ni})_6\text{Sn}_5\) IMC was also affected by cooling condition. In samples reflowed at 275 °C for 1 s, when the cooling rate was fast, the \((\text{Cu,Ni})_6\text{Sn}_5\) IMC was almost needle-type with a hexagonal cross-section. On the other hand, when the cooling rate was slow, the size of the \((\text{Cu,Ni})_6\text{Sn}_5\) IMC became lager, and cylinder-type IMCs with a hexagonal cross-section and pointed tips formed at the interface. Even though the morphology of the IMC changed with the reflow and cooling conditions, these all IMCs had a similar chemical composition. The composition of these \((\text{Cu,Ni})_6\text{Sn}_5\) IMCs was 30.6–43.7 at.%Cu, 11.9–20.8 at.%Ni and 43.8–48.6 at.%Sn. The results of this study imply that the conditions of reflow and cooling in the reflow process must be strictly controlled to produce the desired IMC layer at the interface.

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