

## TRANSIENT LIQUID PHASE BEHAVIOR OF Sn-COATED Cu PARTICLES AND CHIP BONDING USING PASTE CONTAINING THE PARTICLES

Sn-coated Cu particles were prepared as a filler material for transient liquid phase (TLP) bonding. The thickness of Sn coating was controlled by controlling the number of plating cycles. The Sn-coated Cu particles best suited for TLP bonding were fabricated by Sn plating thrice, and the particles showed a pronounced endothermic peak at 232°C. The heating of the particles for just 10 s at 250°C destroyed the initial core-shell structure and encouraged the formation of Cu-Sn intermetallic compounds. Further, die bonding was also successfully performed at 250°C under a slight bonding pressure of around 0.1 MPa using a paste containing the particles. The bonding time of 30 s facilitated the bonding of Sn-coated Cu particles to the Au surface and also increased the probability of network formation between particles.

*Keywords:* Sn-coated Cu, immersion plating, chip bonding, transient liquid phase (TLP) sintering, intermetallic compounds (IMC)

### 1. Introduction

With the extensive application of power modules containing silicon carbide (SiC) chips, the need for bonding materials that can withstand extremely high operating temperatures and do not melt has increased [1]. Although high-temperature solder alloys are preferential candidates, they are not used in the electronics industry due to their high-temperature bonding conditions, reliability issues, and absence of unique properties [2]. Ag nanoparticles, though very popular in the electronics industry, require very long sintering durations at temperatures of around 250°C [3]. In addition, a transient liquid phase (TLP) bonding method using a solder layer such as Sn sandwiched between high conductive and cost-effective metal layers such as Cu is considered to be an alternative method that can possess sufficient reliability [4-6]. The solder melted at an appropriate temperature reacts with Cu to form intermetallic compounds (IMC), which are capable of withstanding temperatures higher than the reaction temperature. However, the TLP bonding requires high temperature and long bonding time. For example, to transform the molten Sn layer into solid intermetallic layers in the sandwiched bondline, the bonding time required at 340°C was 90 min.

In this study, chip bonding was conducted by TLP sintering using Sn-coated Cu particles. Significantly, when compared to earlier TLP bonding methods [7], the inclusion of particles results in the formation of a relatively uniform bondline structure at low magnification. Moreover, the core/shell particles will remarkably decrease the TLP bonding time at relatively low temperature

because particles with this structure can reduce the time required for the completion of the reaction between molten Sn and Cu.

### 2. Materials and methods

Sn coating on spherical Cu particles was accomplished using immersion plating. To prepare the Sn plating solution, 0.0158 mol of tin(II) chloride (SnCl<sub>2</sub>, Sigma-Aldrich, 98%) and 0.0788 mol of thiourea (SC(NH<sub>2</sub>)<sub>2</sub>, Samchun chemicals, 98%) were added to 50 mL of ethylene glycol ((CH<sub>2</sub>OH)<sub>2</sub>, 99.7%, SK networks). All the chemicals were mixed in a beaker by stirring, on a hot plate maintained at 65°C. Meanwhile, 5 g of spherical Cu powder (99.64%, average particle size: 2 μm, JoinM) was dispersed at 65°C in 50 mL of ethylene glycol in another beaker; once the particles were dispersed well, the Cu powder solution was added to the plating solution and the mixture was continuously stirred for 5 min at 65°C. Further, the plating step was performed once, twice, and thrice to obtain particles with Sn shells of different thicknesses. After sedimentation of the plated particles, the supernatant was decanted off and the beaker was refilled with distilled water. This step of decantation and washing with distilled water was repeated three times. The sediment was collected and washed with ethyl alcohol, followed by drying in a vacuum chamber.

The cross-sectional microstructure of the fabricated Sn-coated Cu particles was observed with scanning electron microscopy (SEM, VEGA 3 LMU, TESCAN Ltd.) using the back-scattered electron (BSE) mode. While energy-dispersive

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spectroscopy (EDS, 4502A-3UES-SN, Thermo) was used to analyze the composition of the fabricated particles, differential scanning calorimetry (DSC, Q20, TA Instruments, Inc.) was used to analyze their thermal characteristics. The content variation of elements within a cross-section of the sample was verified using a field emission electron probe micro analyzer (EPMA, JXA-8530F, JEOL Ltd). In order to understand the phase transformation during heating, X-ray diffraction (XRD, D 8 Focus, Bruker AXS GMBH) was also conducted.

A paste was prepared by mixing the Sn-coated Cu particles with a commercial flux (KS-ST22, Koki Korea Co, Ltd.) at a 9:1 ratio. This paste was then sandwiched between an Au-plated substrate and an Au-plated chip, in order to achieve chip bonding.

### 3. Results and discussions

Figure 1 shows cross-sectional BSE images of Sn-coated Cu particles prepared using different numbers of plating cycles.

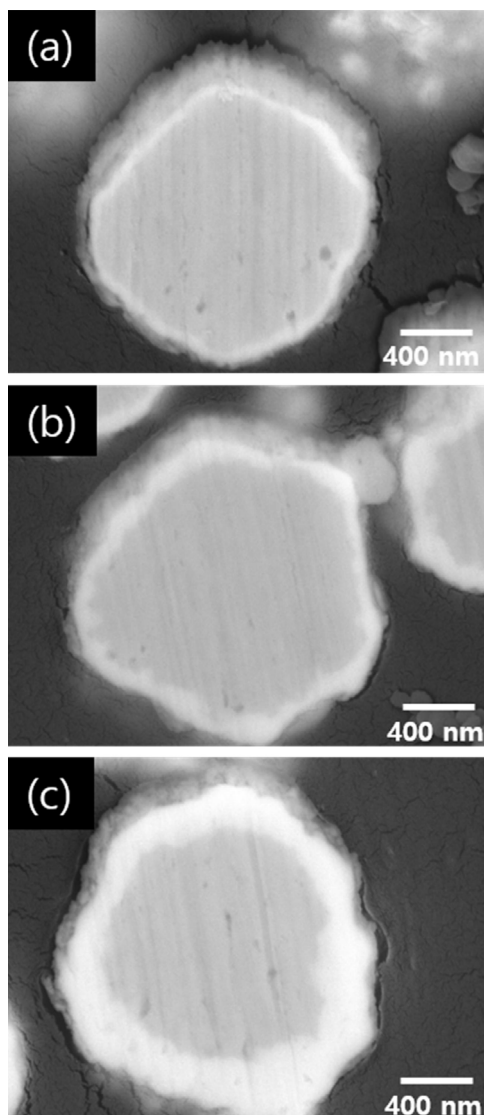


Fig. 1. Cross-sectional BSE images of Sn-coated Cu particles prepared with different number of plating cycles: (a) 1 time, (b) 2 times, and (c) 3 times

While the gray region at the core indicates a pure Cu phase, the white region at the edge represents a pure Sn phase. The images clearly show that an increase in the number of plating cycles increases the thickness of Sn shell around the Cu particles. Moreover, the thicknesses of the Sn shells formed around the Cu core were fairly uniform.

Figure 2 shows the thickness of the Sn coating and the Sn content (in wt%) of the synthesized particles prepared with different number of plating cycles. The shell thicknesses of ten particles were measured using cross-sectional BSE images and an average value was calculated. The Sn content of each synthesized sample was determined by conducting five EDS measurements for each synthesized sample at  $\times 3000$  magnification. However, the determined Sn content is likely to be slightly over-estimated since EDS measurements are meant for surface materials only. The results showed that the coating thickness and the Sn content increased linearly with the number of plating cycles.

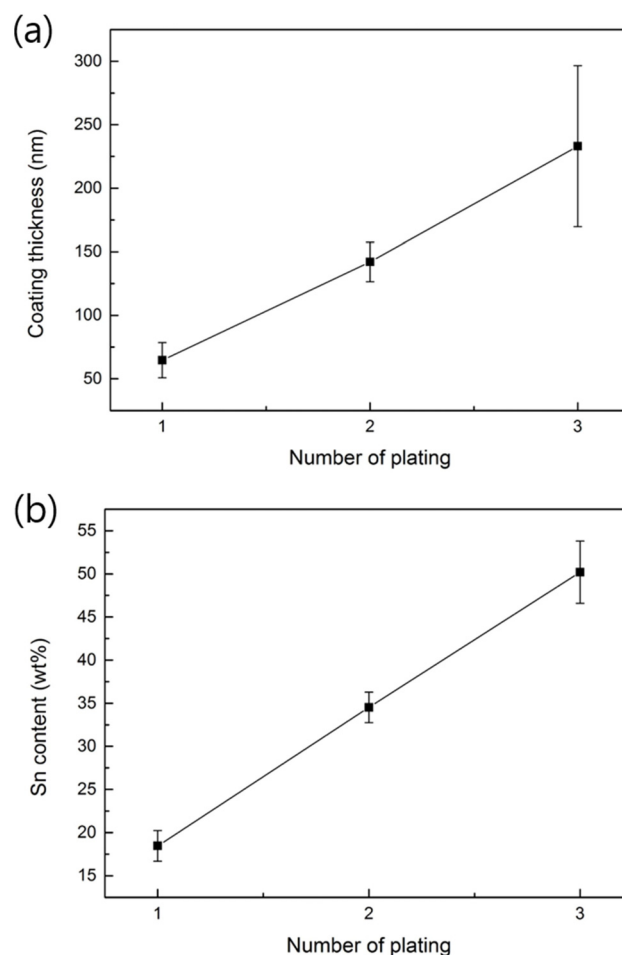


Fig. 2. (a) Sn coating thickness and (b) Sn content in Sn-coated Cu particles prepared with different number of plating cycles

The DSC curves of Sn-coated Cu particles prepared with different number of plating cycles during the first and second heating cycles are displayed in Fig. 3. The heating rate was  $20^{\circ}\text{C}/\text{min}$ . During the first heating cycle (Fig. 3a), the Sn-coated Cu particles that were plated once showed the formation of a marginal exothermic peak at  $98^{\circ}\text{C}$  and a large and slightly broad

exothermic peak at 162°C. The Sn-coated Cu particles that were plated twice exhibited the formation of a minor, marginal exothermic peak at 98°C and a large exothermic peak at 149°C. Finally, the Sn-coated Cu particles that were plated thrice also showed a minor exothermic peak at 98°C and a large exothermic peak at 149°C. The first minor exothermic peak formed at 98°C is thought to arise due to the reaction between the Sn coating and the Cu core. The reaction between Sn and Cu preferentially forms the intermetallic  $\text{Cu}_6\text{Sn}_5$  and releases the exothermic enthalpy of formation [7,8]. These peaks were observed at 98°C irrespective of the thickness of Sn coating. However, their sizes greatly depended on the thickness of the Sn shell because the amount of Sn reacting with Cu is extremely small in the case of the thin Sn shell. The second major exothermic peak is thought to arise due to continuing  $\text{Cu}_6\text{Sn}_5$  formation and  $\text{Cu}_3\text{Sn}$  formation via the reaction of the formed  $\text{Cu}_6\text{Sn}_5$  with the Cu core. The formation of the  $\text{Cu}_3\text{Sn}$  phase generates more heat than that of  $\text{Cu}_6\text{Sn}_5$  [8]. The temperature at which this second peak was observed decreased from 162°C to 149°C with an increase in Sn thickness. Significantly, the  $\text{Cu}_3\text{Sn}$  phase is produced after  $\text{Cu}_6\text{Sn}_5$  formation. Hence, this result implies that the formation temperature of the  $\text{Cu}_3\text{Sn}$  phase may increase if the thickness of the  $\text{Cu}_6\text{Sn}_5$  phase is small.

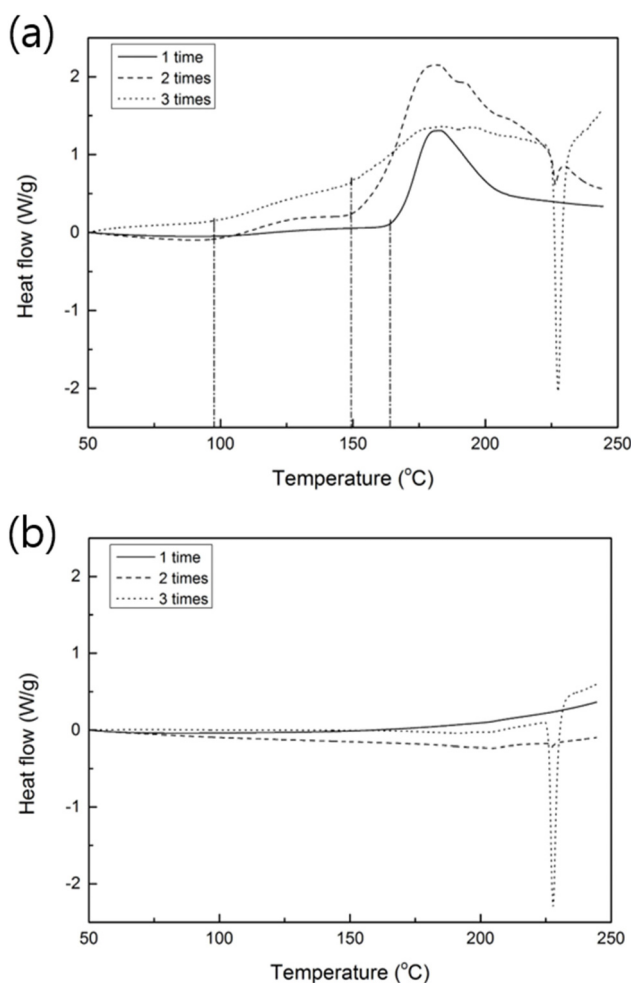


Fig. 3. DSC curves of Sn-coated Cu particles prepared at three different plating conditions, during the first heating (a) and second heating (b) cycles

The most significant result observed was the presence of the endothermic peaks at 232°C (the melting point of Sn). This peak was not observed in the case of once-plated particles. However, a small peak was observed in the case of twice-plated particles. For thrice-plated particles, a remarkably pronounced endothermic peak was observed at 232°C, indicating that a significant amount of pure Sn shell was still remained. These results indicate that the Sn-coated Cu particles that were plated thrice retain a sufficient amount of pure Sn and could be used for soldering during chip bonding.

During the second heating cycle (Fig. 3b), none of the exothermic peaks were observed and the endothermic peaks at 232°C were measured. The endothermic peak for the twice-plated sample was very small. However, the endothermic peak for the thrice-plated sample was still extremely pronounced, indicating that the amount of pure Sn for soldering was abundant. Hence, all further experiments were performed only with the Sn-coated Cu particles that were plated thrice.

The cross-sectional BSE images and the line profiles of Sn-coated Cu particles produced using field-emission EPMA after heating at 250°C with different numbers of plating cycles are shown in Fig. 4. Figure 4a clearly shows the core/shell structure of Cu/Sn in both the BSE image and the line profile. The Sn and Cu contents of similar intensity are observed at the Sn/Cu interface, indicating the formation of a small amount of Cu-Sn intermetallic compound. The Sn line profile abruptly changed after 10 s at 250°C, as seen in Fig. 4b. The previous Sn profile has been replaced with a new Sn profile that overlaps with the Cu profile. Thus, Fig. 4b confirmed the disappearance of the initial core-shell structure. A dimple-shaped structure was observed at the center of the new Sn profile. This could indicate the coexistence of intermetallic  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$ . However, a closer analysis could not be carried out to determine the nature of the intermetallic phase due to the SEM resolution limit. Also, the dimple-shaped Sn profile for the sample that was heated for 30 s (Fig. 4c) completely vanished. It is believed that this phenomenon is observed because the  $\text{Cu}_6\text{Sn}_5$  phase has been transformed into the  $\text{Cu}_3\text{Sn}$  phase in the center of the Cu particle. The samples heated for 60 s (Fig. 4d) and 120 s (Fig. not shown) exhibited no noticeable changes.

The XRD results of Sn-coated Cu powder heated at 250°C at different times are as shown in Fig. 5. Trace amounts of  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  intermetallic compounds as well as Sn and Cu were recorded. As reaction time approached 10 s, the main peaks of Sn and Cu almost disappeared and a prominent  $\text{Cu}_6\text{Sn}_5$  peak and an inconspicuous  $\text{Cu}_3\text{Sn}$  peak appeared. The main peak of  $\text{Cu}_3\text{Sn}$  became more defined and pronounced when the reaction time increased to 30 s. These results show the possibility of using these synthesized Sn-coated Cu particles (plated thrice) for rapid chip bonding by TLP. The relative intensity of the  $\text{Cu}_3\text{Sn}$  peak increased when the reaction time was increased to 60 s or 120 s. These results demonstrate that, with the increase in the reaction time from 10 s to 120 s, the preferentially formed intermetallic  $\text{Cu}_6\text{Sn}_5$  gradually transforms into  $\text{Cu}_3\text{Sn}$ .

Finally, die bonding was performed using a paste that mainly contained the Sn-coated Cu powder. Figure 6 shows the

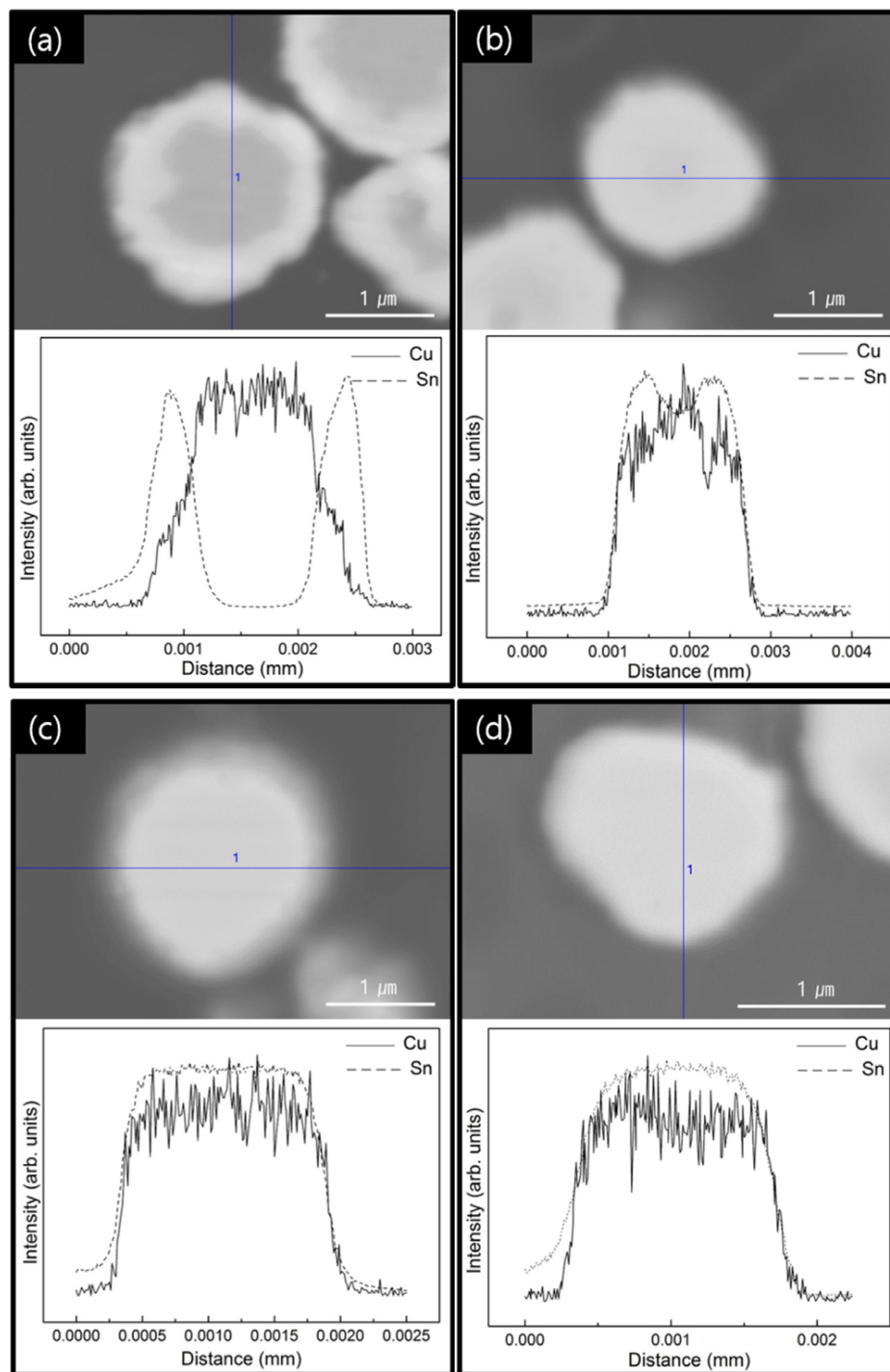


Fig. 4. Cross-sectional BSE images and line profiles of Sn-coated Cu particles obtained using field-emission EPMA after heating at 250°C for different durations: (a) as-prepared, (b) 10 s, (c) 30 s, and (d) 60 s

cross-sectional BSE images of bondlines formed after die bonding at 250°C using a slight bonding pressure of around 0.1 MPa at different heating times. Both the die and substrate were plated with Au. The paste solidified abruptly after heating at 250°C. When the Sn-coated Cu particles were heated for 10 s, there was no indication of extensive physical network formation or a connection between the particles and the Au surfaces. This unpredictable outcome could be a result of the TLP sintering process failing to be completed. Owing to the low thermal conductivity of the paste, the heating time of 10 s may be insufficient to melt

Sn. This interpretation can be verified from the fact that most Sn-coated Cu particles maintained the core-shell structure even after the heating for 10 s. However, when the heating time was increased to 30 s, the bonding of Sn-coated Cu particles to the Au surface and connections between particles were simultaneously achieved. The microstructure was continuously monitored and no notable microstructural changes were observed when the heating time was changed from 30 s to 120 s. When compared to results in Fig. 4 and 5, a major discrepancy in the microstructure of Sn-coated Cu particles was observed: i.e., even after heating,

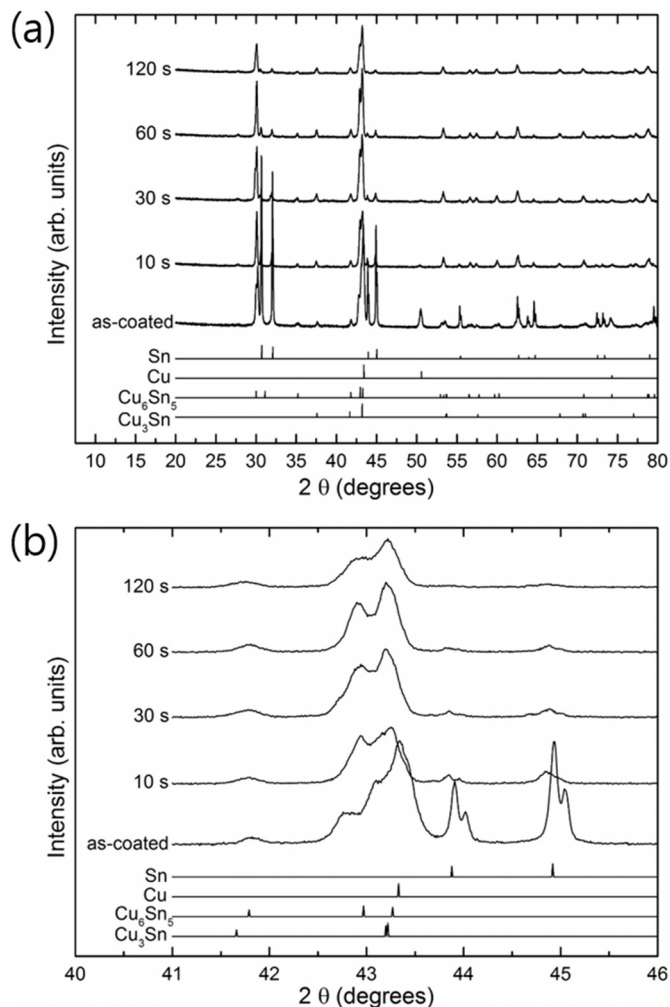


Fig. 5. XRD results of Sn-coated Cu powder heated at 250°C for different durations: (a) full-scan range of 20°-80° and (b) magnification narrow range of 41°-46°

some particles maintained their core-shell structure. The Sn shell converted to the  $\text{Cu}_6\text{Sn}_5$  phase immediately after melting, similar to previous results. However, unlike the conditions seen in Fig. 4 and 5, the Sn in the  $\text{Cu}_6\text{Sn}_5$  diffused not only into the original Cu core but also to the newly connected neighboring particles formed due to the extended structure of the network. Thus, Sn diffused in all directions from the Cu core to each and every point of the linked Sn shells. This diluted diffusion of Sn greatly reduced the growth rate of  $\text{Cu}_6\text{Sn}_5$  phase and increased the time required to deplete the Cu core. The core-shell structures were also dominant among the Sn-coated Cu particles that were bonded to the Au surface. This was due to the depletion of Sn caused by the reaction with Au to form  $\text{AuSn}_4$  intermetallic compound.

#### 4. Conclusions

The Sn-coated Cu particles were successfully synthesized using the proposed wet plating method. The particles best suited for the TLP sintering process were prepared by plating

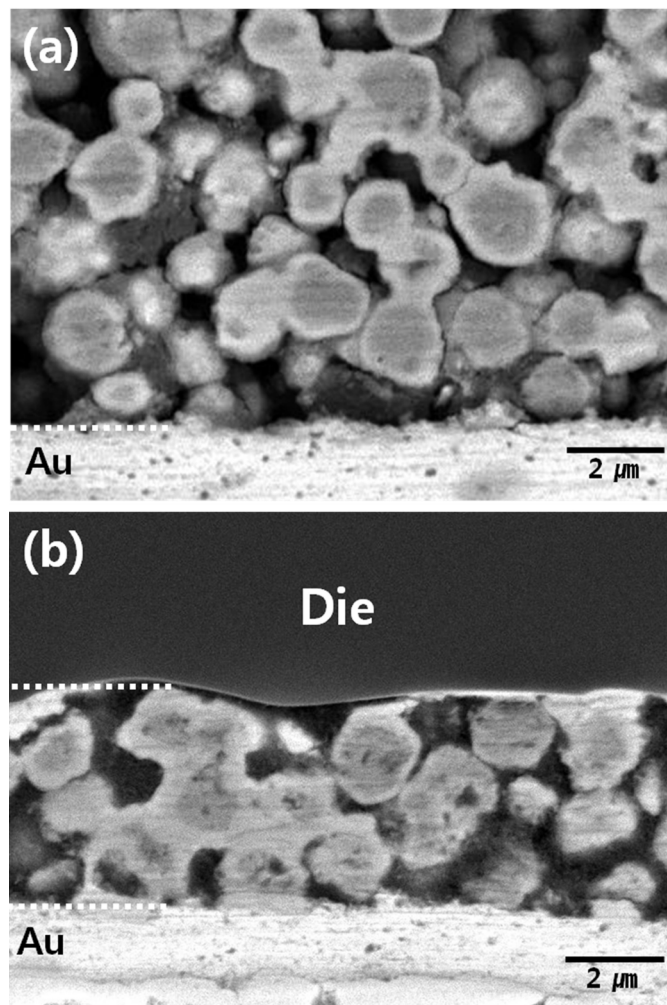


Fig. 6. Cross-sectional BSE images of bondlines formed after die bonding using a Sn-coated Cu paste at 250°C for different heating durations: (a) 10 s and (b) 30 s

Cu particles with Sn three times. DSC measurements showed that the reaction between the Sn shell and Cu core initiates at 98°C and subsequent reactions take place at 149°C at an accelerated pace. Moreover, a striking endothermic peak at 232°C was also observed, which confirmed the formation of sufficient amount of Sn. It was also interesting to note that heating of Sn-coated Cu particles for just 10 s at 250°C destroyed the initial core-shell structure and encouraged the formation of Cu-Sn intermetallics. The die bonding was also successfully performed at 250°C under the bonding pressure of around 0.1 MPa using a paste mainly containing the Sn-coated Cu powder. In contrast to the results obtained when Sn-coated Cu particles were directly heated, indirect heating for 10 s through the paste did not result in the formation of microstructures of the bondline, due to insufficient TLP sintering. Increasing bonding time to 30 s facilitated the bonding of Sn-coated Cu particles to the Au surface and also increased the probability of network formation between particles.

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**REFERENCES**

- [1] J. Yin, Z. Liang, J.D. Wyk, *IEEE Trans. Power Electron.* **22**, 392 (2007).
- [2] J.E. Lee, K.S. Kim, K. Suganuma, J. Takenaka, K. Hagio, *Mater. Trans.* **46**, 2413 (2005).
- [3] E. Halonen, T. Viiru, K. Östman, A.L. Cabezas, M. Mäntysalo, *IEEE Trans. Compon. Packag. Manuf. Technol.* **3**, 350 (2013).
- [4] N.S. Bosco, F.W. Zok, *Acta Mater.* **53**, 2019 (2005).
- [5] J.F. Li, P.A. Agyakwa, C.M. Johnson, *Acta Mater.* **59**, 1198 (2011).
- [6] M.S. Park, S.L. Gibbons, R. Arróyave, *Acta Mater.* **60**, 6278 (2012).
- [7] W. Gierlotka, S.W. Chen, S.K. Lin, *J. Mater. Res.* **22**, 3158 (2007).
- [8] H. Flandorfer, U. Saeed, C. Luef, A. Sabbar, H. Ipsler, *Thermochim. Acta* **459**, 34 (2007).