



# Transient Liquid Phase Bonding Process Using Sn-coated Cu Dendritic Particles

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Received: 28 August 2019 / Accepted: 16 March 2020 / Published online: 7 April 2020  
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## Abstract

To reduce bonding time in the die bonding process of power devices, we propose a novel technique based on the melting and reactions of Sn shells in Sn-coated Cu dendritic particles during heating. In this study, transient liquid phase (TLP) die bonding was performed at 250 °C in air under 10 MPa of pressure. Sn coating content was considered as a main process parameter. During the immersion Sn plating (coating) of Cu dendritic particles, excessive Cu<sub>6</sub>Sn<sub>5</sub> and Sn were formed in situ. Coating the Cu dendritic particles significantly reduced the oxidation of core Cu during heating in air. When the average Sn coating content was 18 wt%, abundant Cu remained based on Sn shortages, even after 10 min of reaction. However, pure Cu was virtually eliminated in the bondlines following an identical reaction when the Sn content was 45 wt%. A paste containing 45 wt% Sn-coated Cu dendritic particles provides more effective TLP bondability, resulting in average shear strengths of bondlines of 19.6 and 21.4 MPa following die bonding for 3 and 5 min, respectively.

**Keywords** Sn-coated Cu · Dendritic particle · Sinter-bonding · Die-attach · Shear strength

## 1 Introduction

Based on insistent changes to silicon carbide devices to enhance conversion efficiency in power modules, the need for bonding materials that can withstand high operating temperatures in the range of 250–300 °C has been steadily increasing [1–3]. Considering the homologous temperatures of bonding materials at common operating temperatures, conventional soldering techniques must be replaced with updated processing methods that provide significantly higher melting temperatures. As a representative alternative, the transient liquid phase (TLP) bonding method using a Sn layer sandwiched between highly conductive and cost-effective metal layers, such as Cu, is considered to be a feasible solution [4–7]. The Sn layer, which is melted during heating to achieve bonding, reacts with Cu to form intermetallic compounds (IMCs), which are capable of tolerating temperatures greater than the reaction temperature. However, TLP bonding requires long bonding times at high temperatures.

For example, to transform a sandwiched structure of Cu/molten Sn/Cu layers into a solid intermetallic bondline, the required bonding time at 340 °C has been reported to be 90 min [5].

In this study, chip bonding was performed via TLP sintering using Sn-coated Cu dendritic particles to reduce bonding time significantly with enlargement in reaction area of the Sn/Cu interfaces at a slightly higher temperature (250 °C) than the melting point of Sn (232 °C). When compared to the conventional TLP bonding method [5, 7], the vast interface area between Sn/Cu in the Sn-coated Cu dendritic particles in the proposed method, as well as the complete consumption of Sn and Cu separated into small fragments, is expected to dramatically reduce TLP bonding time following the melting of Sn.

## 2 Experimental Procedure

The Sn coating of Cu dendritic particles was accomplished using an immersion plating method. First, 5 g of Cu dendritic powder, which was synthesized in-house, was dispersed in 50 mL of ethylene glycol [(CH<sub>2</sub>OH)<sub>2</sub>, 99.7%, SK Networks] in a beaker. To prepare the Sn plating solution, 3.0 g of tin(II) chloride (SnCl<sub>2</sub>, 98.0%, Daejung Chemical)

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and 6.0 g of thiourea [ $\text{CS}(\text{NH}_2)_2$ , 98.0%, Daejung Chemical] were dissolved in 50 mL of ethylene glycol in another beaker. The tin(II) chloride solution was then poured into the Cu powder solution, and the resulting mixture was stirred continuously at 250 rpm for 10 min. The Sn content in the Sn-coated Cu powder was controlled by repeating the Sn pouring process. Following the plating process, the particles were rinsed using ethanol three times, followed by drying in a vacuum chamber at room temperature.

Pastes containing dried Sn-coated Cu dendritic particles were prepared by mixing the particles with  $\alpha$ -terpineol ( $\text{C}_{10}\text{H}_{18}\text{O}$ , 98.5%, Samchun Pure Chemical) as a vehicle. The content of  $\alpha$ -terpineol was equal to 60 wt% of the Cu powder. Die bonding was performed using a dummy Cu chip with an area of  $3\text{ mm} \times 3\text{ mm}$  and a dummy Cu substrate with an area of  $10\text{ mm} \times 10\text{ mm}$ . The prepared paste was printed onto the substrates using a stencil mask with a slit volume of  $3\text{ mm} \times 3\text{ mm} \times 0.1\text{ mm}$  and a squeegee. After printing, the chips were aligned on a printed pattern and the sandwich-structured samples were heated to  $250\text{ }^\circ\text{C}$ . Die bonding was performed in an air atmosphere under 10 MPa of pressure throughout the bonding time.

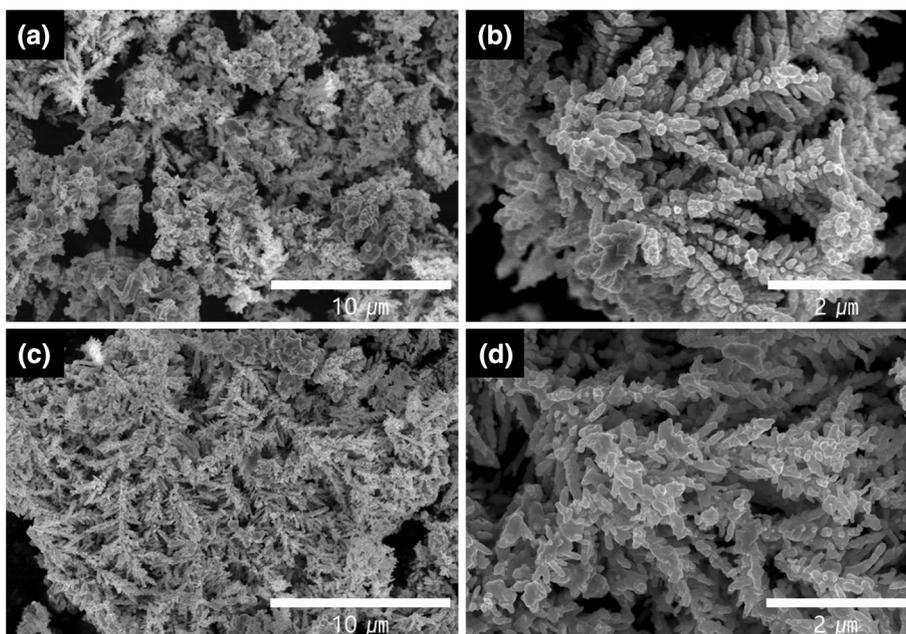
The microstructures of the fabricated Sn-coated Cu dendritic particles, formed bondlines, and fracture surfaces of the bondlines were observed using high-resolution field-emission scanning electron microscopy (SEM, SU-8010, Hitachi). In some cases, the back-scattered electron (BSE) mode was utilized to distinguish the distributions of phases in the bondlines. Energy-dispersive spectroscopy (EDS, 4502A-3UES-SN, Thermo) was used to analyze the compositions of specific phases in the bondlines. To analyze the states of the as-fabricated Sn-coated Cu particles and the

phase transformations during heating in air, X-ray diffraction (XRD, D 8 Focus, Bruker) analysis was also conducted. The quantitative amount of Sn coating was determined using inductively coupled plasma mass spectrometry (ICP-MA, ICAP-Q, Thermo Fisher Scientific). The thermal characteristics of various dendritic particles in air were analyzed using thermogravimetry-differential scanning calorimetry (TG-DSC, Q600, TA Instruments). Heating was conducted up to  $300\text{ }^\circ\text{C}$  at the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . The bonding strength of the joints was defined as the maximum stress value measured during shear testing at  $200\text{ }\mu\text{m}/\text{s}$  at a distance of  $200\text{ }\mu\text{m}$  from the bottom.

### 3 Results and Discussion

Figure 1 presents the microstructures of Sn-coated Cu dendritic particles fabricated with different Sn contents. The shape of the as-synthesized Cu particles after 5 min is a rice-ear shape with well-developed fractal structures at every tip site [8]. However, the clarity of the fractals is reduced by the formation of blunt tips and uniformity is partially distorted following Sn plating. Because the mechanism of Sn plating is a replacement reaction, microstructural changes are inevitable. Thiourea, which is a complexing agent used to decrease the equilibrium electrode potential of Cu to a lower value than that of Sn, can form  $[\text{Cu}(\text{NH}_2\text{CSNH}_2)_4]^+$  complex ions, which have greater stability than  $[\text{Cu}(\text{NH}_2\text{CSNH}_2)_4]^{2+}$  [9, 10]. Therefore, in this system,  $\text{Cu}^+$  is more prominent as an oxidation product of Cu [11, 12]. The  $\text{Cu}^+$  in the solution reduces the amount of  $\text{Sn}^{2+}$  through the replacement reaction of  $2\text{Cu}^+ + \text{Sn}^{2+} \rightarrow 2\text{Cu}^{2+} + \text{Sn}$ , which induces substantive

**Fig. 1** a, c Low- and b, d high-magnification SEM images of Sn-coated Cu dendritic particles fabricated with different Sn contents: a, b 18 wt% and c, d 45 wt%



erosion on the surfaces of the Cu dendritic particles. Additionally, the deposition rate of Sn plating may slow with a decrease in the amount of  $\text{Cu}^+$  and halt with completion of conformal Sn coating. Therefore, Sn deposition following conformal coating can only be sustained by diffusing Cu into the plated Sn layer.

Regardless, the main structure of the rice-ear shapes is maintained following Sn plating, resulting in a large surface area. Figure 1a, b present representative shapes of Cu dendritic particles coated with 18 wt% and 45 wt% Sn, respectively. Although the tips become increasingly blunt and the rice-ear shapes become more severely aggregated with increasing Sn content, minor aggregation seems to be reversed during the subsequent mixing process to prepare the paste. The Sn content values were determined via ICP-MA measurement.

Figure 2 presents XRD patterns of Sn-coated Cu dendritic particles fabricated with different Sn contents. The results confirm the existence of Cu–Sn IMCs (especially  $\text{Cu}_6\text{Sn}_5$ ), as well as Sn and Cu [13]. With increasing Sn content, the intensities of the Cu peaks decrease and those of the pure Sn and  $\text{Cu}_6\text{Sn}_5$  peaks increase, indicating that the IMC phase develops during Sn plating. The formation of a  $\text{Cu}_6\text{Sn}_5$  IMC phase during plating corresponds to the aforementioned mechanism (diffusion of Cu into a plated Sn layer) for sustained Sn deposition.

Cross-sectional images of the bondlines resulting from TLP bonding at 250 °C using 18 wt% Sn-coated Cu dendritic particles are presented in Fig. 3. Although a few large voids can be observed based on melting of the Sn coating, various phases were detected together in the bondlines. Because the images were captured in BSE mode, the differences between light and dark areas may signify the domains of different phases. The compositions of specific domains, which are indicated by the achromatic colors of identical brightness,

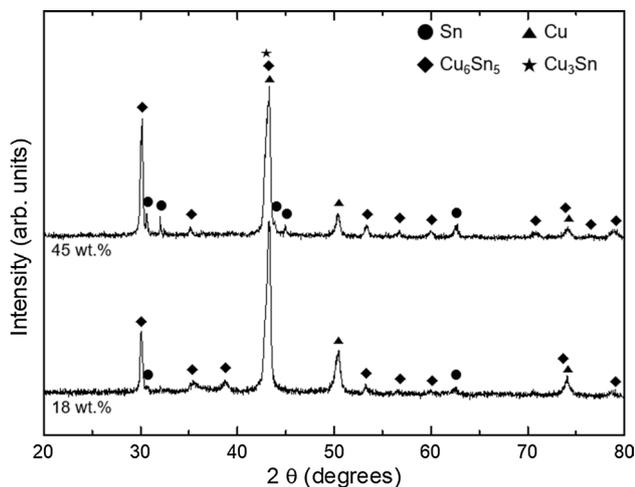
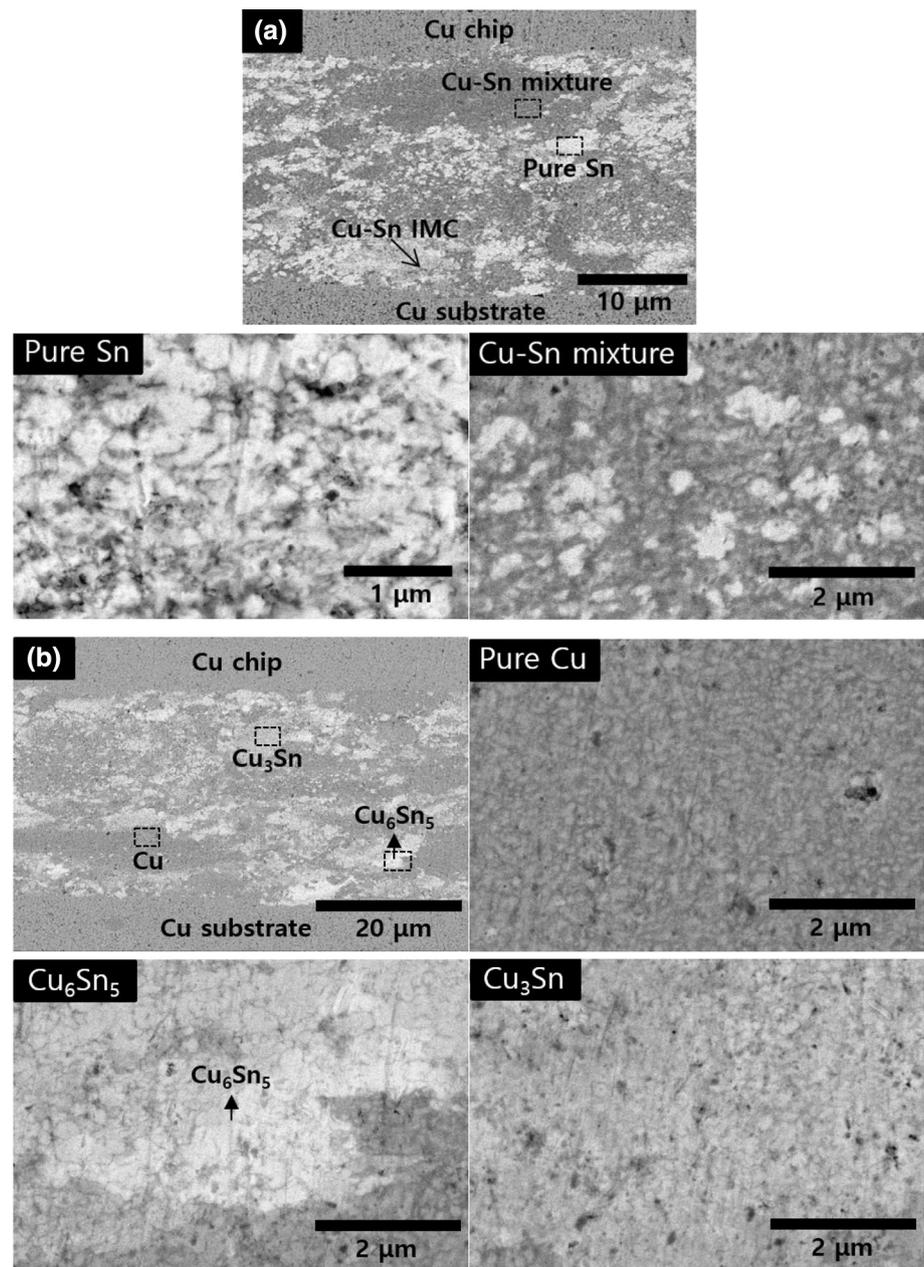


Fig. 2 XRD patterns of as-fabricated Sn-coated Cu dendritic particles

were confirmed by EDS measurements. When bonding was performed for 3 min (Fig. 3a), three different phases were observed: dark grey for Cu, white for pure Sn, and light grey for Cu–Sn IMC ( $\text{Cu}_6\text{Sn}_5$ ). In the Cu–Sn mixture region, unreacted Cu and Sn are finely distributed with the Cu–Sn IMC. When increasing the bonding time to 10 min (Fig. 3b), the remnant phases change significantly. Pure Sn largely disappears and two IMCs of  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  are clearly visible in addition to pure Cu. This indicates that prolonged bonding time promotes reactions between Sn and Cu, eventually leading to a shortage of Sn. To form the final equilibrium phase of  $\text{Cu}_3\text{Sn}$ , 61.8 wt% of Cu and 38.2 wt% of Sn are required [14]. Therefore, a Sn shortage is considered to be inevitable during TLP bonding using 18 wt% Sn-coated particles. However, homogeneous mixing between Sn and Cu should significantly reduce the extinction time of Sn. The remaining Sn in Fig. 3a can be attributed to delayed reactions caused by inhomogeneous mixing between Sn and Cu, as well as oxide layers on the Sn surfaces. Because preferentially generated  $\text{Cu}_6\text{Sn}_5$  IMCs are formed via nucleation based on the dissolution of Cu atoms into molten Sn [15], the extinction of pure Sn is accelerated. In contrast, the transformation from  $\text{Cu}_6\text{Sn}_5$  to  $\text{Cu}_3\text{Sn}$  is relatively slow based on the process of solid-state diffusion. Furthermore, inhomogeneous mixing can lead to microstructural inhomogeneity in the final bondlines.

Figure 4 presents cross-sectional images of the bondlines resulting from TLP bonding at 250 °C using 45 wt% Sn-coated Cu dendritic particles. In the sample bonded for 3 min,  $\text{Cu}_3\text{Sn}$  IMCs are prevalent and pure Sn is rare in the bondlines. Minor phases of pure Cu and  $\text{Cu}_6\text{Sn}_5$  are distributed in small patches. Despite identical reaction conditions compared to those discussed above, the Sn extinction time decreases with the greater Sn content of 45 wt%, indicating that increased Sn content can induce more homogeneous reactions based on the contribution of capillary flows following Sn melting. When increasing the bonding time to 10 min, the microstructures of bondlines become denser based on decreasing bondline thickness, although the pure Cu and  $\text{Cu}_6\text{Sn}_5$  phases to remain. As mentioned previously, the transformation into a perfectly uniform  $\text{Cu}_3\text{Sn}$  phase following the disappearance of molten Sn is an extremely time-consuming process. Furthermore, it is likely that excessive Sn content (45 wt%) above 38.2 wt% is favorable for accelerating Sn elimination and the formation of IMC-based bondlines under imperfect mixing conditions between Sn and Cu. In summary, TLP bonding for 3 min using 45 wt% Sn-coated Cu dendritic particles results in the elimination of Sn, which is the phase with the lowest melting point, and bonding for 5 min generates a dense microstructure of IMC-based bondlines based on the faster reaction rate brought about by large reaction areas between Sn and Cu inside fractal structures. In the normal process at 250 °C using a Sn

**Fig. 3** Cross-sectional BSE images of the bondlines formed at 250 °C using 18 wt% Sn-coated Cu dendritic particles with different bonding times: **a** 3 min and **b** 10 min



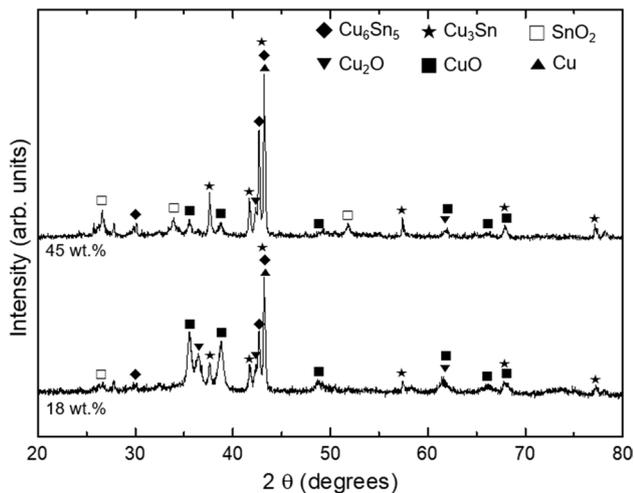
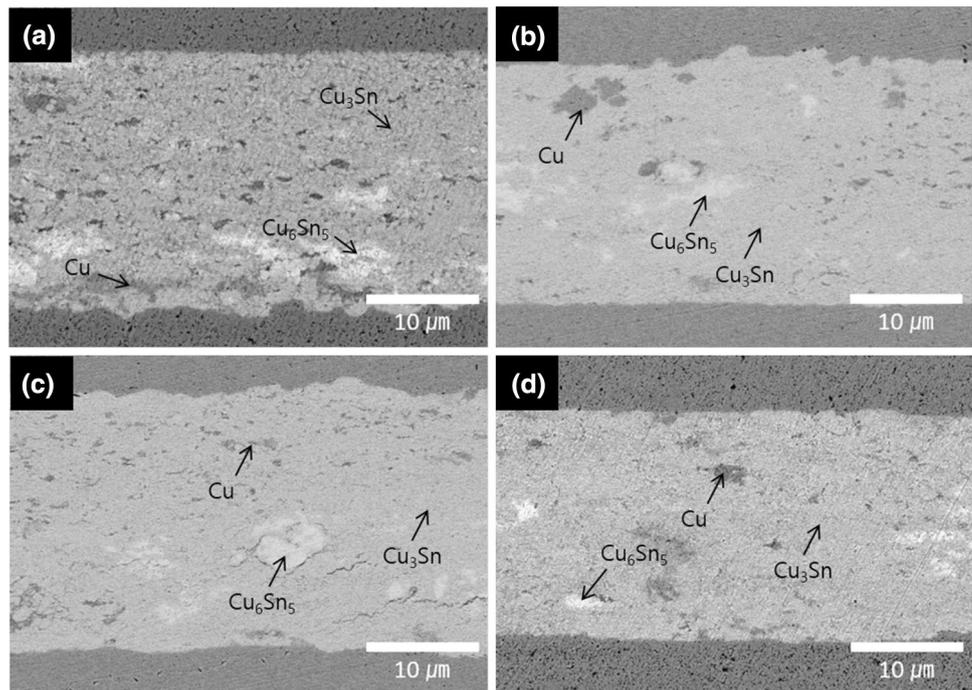
layer, required time for the elimination of Sn was 120 min [7]. Therefore, a TLP bonding method using Sn-coated Cu dendritic particles provides a tremendously fast phase transformation to IMC and completely different microstructures from a layered structure by the normal process.

XRD results for Sn-coated Cu powder heated at 250 °C for 10 min in air are presented in Fig. 5. For the sample with 18 wt% Sn coating, the intensities of the Cu and Cu<sub>6</sub>Sn<sub>5</sub> peaks generally decrease, while those of the Cu<sub>3</sub>Sn peaks increase. The formation of Cu oxides (Cu<sub>2</sub>O and CuO) and Sn oxide (SnO<sub>2</sub>) can also be observed based on the oxidation in air. The existence of pure Sn cannot be observed. When the Sn content increases to 45 wt%, the intensities of the

Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> peaks increase significantly and that of a Cu peak decrease. Although the formation of Cu oxide can also be observed, the intensities of both the Cu<sub>2</sub>O and CuO peaks are relatively small, implying that a thick Sn coating is more effective for suppressing the oxidation of Cu. Additionally, the real amounts of oxides observed in both Sn-coated Cu samples may decrease in the bondlines formed by TLP bonding based on the high density of the bondlines caused by applying external pressure and the shielding effects of dummy chips.

The TG-DSC curves of pure Cu and Sn-coated Cu dendritic particles are presented in Fig. 6. For the pure Cu particles, significant increases in both heat flow and the weight

**Fig. 4** Cross-sectional BSE images of the bondlines formed at 250 °C using 45 wt% Sn-coated Cu dendritic particles with different bonding times: **a** 3 min, **b** 5 min, **c** 7 min, and **d** 10 min

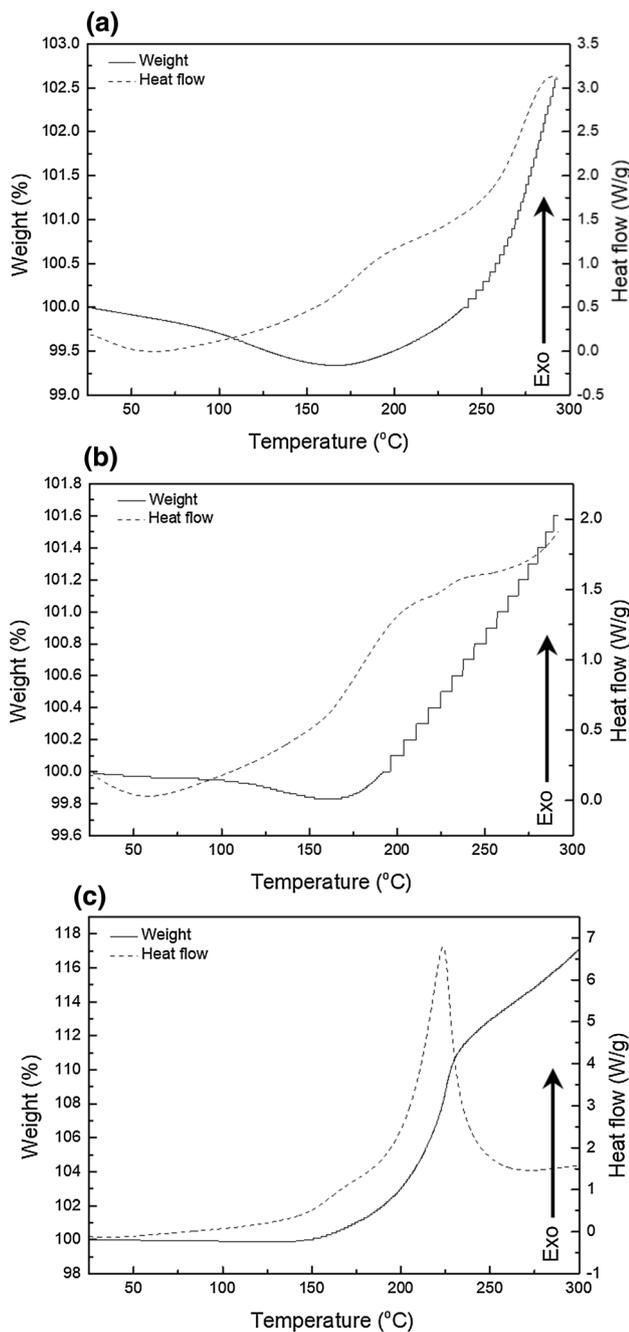


**Fig. 5** XRD patterns of Sn-coated Cu dendritic particles after the heating at 250 °C for 10 min in air

curves can be observed starting at 150 °C. The slopes gradually increase up to 223 °C. As a result, a significant exothermic peak in the heat flow curve is indexed at 223 °C. The cause of this behavior was determined to be an abrupt oxidation phenomenon in air based on the ignition of pure Cu dendritic particles. The surfaces of the synthesized Cu dendritic particles exhibit well-developed bumpy microstructures based on the agglomeration of nanoparticles [8]. Because each bump is only nanometers in size, agglomerates of bumps may oxidize in air extremely rapidly, which would explain the visually observed ignition phenomenon.

In contrast, no significant exothermic peak can be observed for the Sn-coated Cu dendritic particles. When the Sn coating content is 18 wt%, a slight weight decrease (note the change in scale of the Y axis) up to 170 °C based on the evaporation of organic content and a subsequent increase in both weight and heat flow based on oxidation can be observed. This trend is similar to that of the 45 wt% Sn coated sample, but a weight increase of 2.8% and heat flow increase of 3.1% can be observed for the 18 wt% Sn sample, with a weight increase of 2.1% and heat flow increase of 1.8% for the 45 wt% Sn sample at 300 °C. These results indicate that the oxidation degree of core Cu decreases with an increase in the Sn coating content. In real TLP bonding, as opposed to TG-DSC measurement conditions, the bondlines formed by Sn-coated Cu dendritic particles may yield a decreased oxidation degree because the bondlines are densified by external pressure.

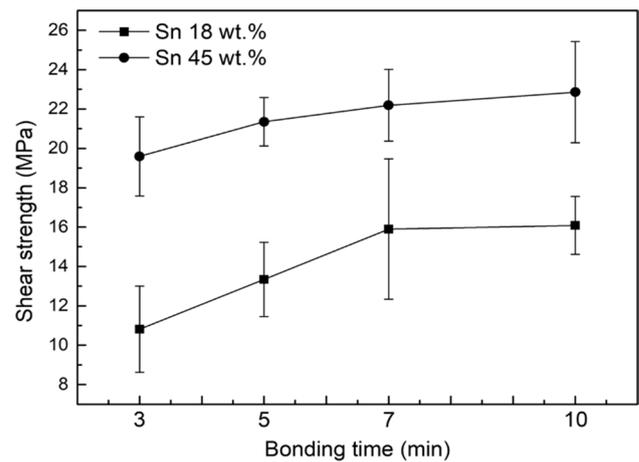
After the die bonding of Cu was performed at 250 °C using a paste containing Sn-coated Cu dendritic particles, the shear strengths of the joints were measured. Figure 7 presents shear strength versus bonding time. For both Sn-coated Cu samples, strength increases with bonding time based on the formation of denser microstructures in the bondlines. However, strength is generally higher for the 45% Sn-coated Cu sample and the initiation of saturation seems to occur earlier for this sample. As representative results, the bonding time of 3 min only yields a strength value approaching 20 MPa, whereas the bonding time of 5 min yields an excellent bonding strength of 21.4 MPa in the case with 45 wt% Sn-coated Cu dendritic particles. In the comparison with



**Fig. 6** TG-DSC curves of **a** pure Cu and Sn-coated Cu dendritic particles prepared with different Sn contents of **b** 18 wt% and **c** 45 wt%

identical bonding temperature, the strength value exceeding 20 MPa in the normal process using a Sn layer was attained after 150 min [7]. Therefore, a performed TLP bonding method indicates extremely fast processability.

Images of the fracture surfaces captured after shear testing are presented in Fig. 8. The fracture surfaces appear to become denser with an increase in bonding time for both Sn-coated Cu samples. However, the densities for the 45 wt%



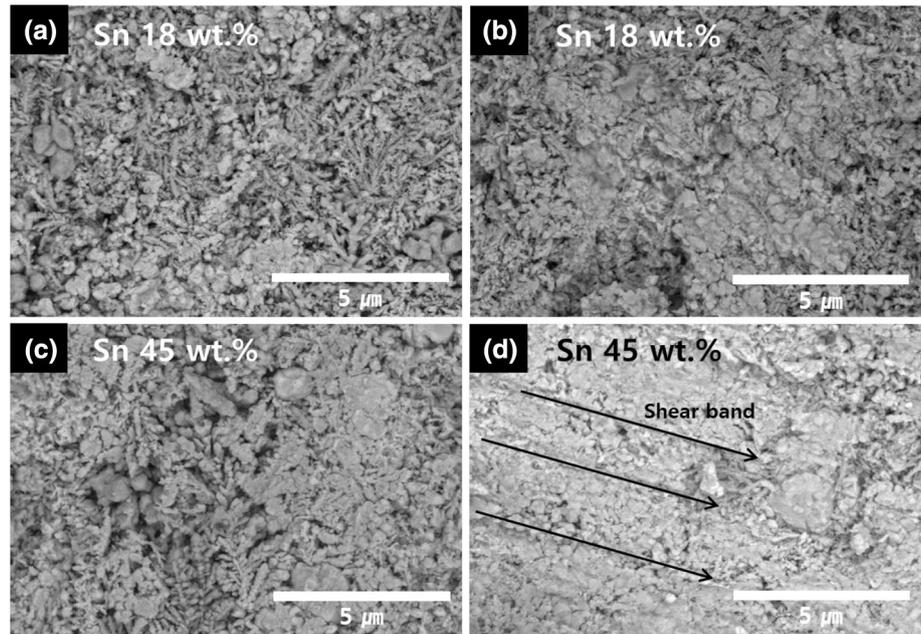
**Fig. 7** Shear strength of the joints formed at 250 °C using Sn-coated Cu dendritic particles as a function of bonding time

Sn-coated Cu samples are noticeably enhanced compared to those of the 18 wt% Sn-coated samples. In particular, a remarkably dense structure can be observed for the heavily sintered sample that was bonded for 10 min using 45 wt% Sn-coated Cu dendritic particles. Therefore, highly developed shear bands are also visible along the fracture surfaces.

## 4 Conclusion

The TLP bonding of a Cu-finished die onto a Cu-finished substrate using a paste containing Sn-coated Cu dendritic particles was successfully performed. The Sn coating of Cu dendritic particles was performed using an immersion plating method. Excessive  $\text{Cu}_6\text{Sn}_5$  phases were formed in situ on the particles during coating. The Sn coating on the Cu dendritic particles significantly reduced the oxidation of core Cu during heating in air. When 45 wt% Sn-coated Cu dendritic particles were used, die bonding times of 3 and 5 min at 250 °C in air under pressure yielded excellent bonding strengths of 19.6 and 21.4 MPa, respectively. With an increase in bonding time, shear strength increased slightly and shear bands on dense microstructures were observed more frequently on the fracture surfaces following shear testing. Because the microstructures along the bondlines contain Cu and  $\text{Cu}_6\text{Sn}_5$  phases in  $\text{Cu}_3\text{Sn}$  matrices, it is anticipated that these bondlines will provide significantly enhanced thermal resistance properties compared to traditional solder alloys. The results of this study demonstrate the feasibility of a 5 min die bonding process using TLP sintering, which implies that semi-continuous die bonding on a conveyor line can be realized.

**Fig. 8** Representative fracture surfaces observed following shear testing with different bonding times: **a, c** 3 min and **b, d** 10 min



**Acknowledgements** This research is supported by "Rediscovery of the Past R&D Result" through the Ministry of Trade, Industry and Energy (MOTIE) and the Korea Institute for Advancement of Technology (KIAT) [Grant No.: P0010211, Project: Development of fundamental mass production (15 kg/batch) technology of copper dendritic powder and continuous silver coating process].

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