Transformation of SAC (Sn3.0Ag0.5Cu) nanoparticles into bulk material during melting process with large melting-point depression

Hyun Jin Kim[1], Seok Pil Jang[2] ✉, Jong-Hyun Lee[3], Yong-Jun Park[4]

[1]*Quality Management Bureau, Defense Agency for Technology and Quality, Changwon Si, Gyeongsangnam-do 51474, Republic of Korea*
[2]*School of Aerospace and Mechanical Engineering, Korea Aerospace University, Goyang, Gyeonggi-do 412-791, Republic of Korea*
[3]*Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea*
[4]*Technology Planning Bureau, Defense Agency for Technology and Quality, Jinju Si, Gyeongsangnam-do 52851, Republic of Korea*
✉ *E-mail: spjang@kau.ac.kr*

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The experimental observation of the transformation of nanosized SAC (Sn3.0Ag0.5Cu) into bulk-sized SAC during the melting process involving a large melting-point depression, using DSC (differential scanning calorimetry) and the reflow test is documented. They manufactured the nanosized SAC in dielectric benzyl alcohol using the modified direct-current arc method. The nanoparticles were spherical in shape with a size distribution of 5–10 nm. Using DSC, the endothermic peaks were continuously measured twice without changing the nanosized SAC. During the initial measurement, they observed peaks at 133, 162 and 217°C. However, in the second cycle, they observed only one peak at 217°C, which indicates the SAC nanoparticles have been completely melted and changed into bulk-sized SAC in the first cycle. They first conducted a reflow test of the SAC nanoparticles suspended in benzyl alcohol including flux on a printed circuit board and a hot plate which are 170°C. It was observed that SAC nanoparticles were transformed into bulk-sized SAC during the melting process at 170°C in less than 3 min. After the melting process, they also observed the formation of thin-layer geometry of SAC with 100 nm and intermetallic Cu_6Sn_5 between the SAC thin layer and a copper plate on PCB.

1. Introduction: Dramatic depression of melting temperature of metals by reducing the size of particles has drawn the attention of many scientists [1–15] because this unique phenomenon has great potential for application in a number of engineering fields. The depressed melting temperature has been reported in many studies by experimental as well as theoretical approaches mainly in research labs [1–15]. Recently, it is an especially daunting challenge to solve the depression of the reflow temperature in microelectronics interconnect technology because the higher reflow temperature requires the more heat to melt the solder that temporarily holds together chips and circuit board in surface-mounting technique; the lead-free Sn-based alloy used in circuit boards has one critical pitfall: a high melting temperature of 215–230°C, compared with the lower melting temperature of eutectic solder materials, 183°C [11]. Therefore many researchers are using nanotechnology to attempt to reduce the particle size of the lead-free Sn-based alloy in order to achieve the depressed melting temperature of the reflow test [7–14]. Although these studies presented the depression of the melting temperature with results measured by differential scanning calorimetry (DSC), they did not observe the complete melting phenomenon at the reflow test with the depression temperature [15, 16]. They just observed the sintering of the nanoparticles at the test.

The issue prompts to us to question whether complete melting with a large melting-point depression, rather than the sintering phenomenon, can be experimentally observed and also whether the characteristics of the transformed metal that results from the nanoparticles would have inherent characteristics that are similar to those of bulk-sized metal, such as melting temperature. In this Letter, we experimentally reported the observation of the transformation of nanosized SAC (Sn3.0Ag5.0Cu) into bulk-sized SAC during the melting process with a large melting depression of 47°C as well as process time less than 3 min using DSC and the reflow test. These results can be helpful to present the direction for solving the depression of the reflow temperature of the lead-free Sn-based solder in microelectronic interconnect technology.

2. Experimental study: We used SAC nanoparticles manufactured by modified direct-current arc (DCA), as presented by Gao *et al.* [14]. In this study, benzyl alcohol with dielectric and antioxidant properties was used as a dielectric protection liquid to minimise the surface oxidation of nanosized SAC. The anode and cathode bars were manufactured with SAC bulk materials and fixed immersing copper bars in the benzyl alcohol. The power (12 mV, 20 A) was supplied to the copper bars and the current arc was generated between the anode and cathode in the benzyl alcohol. The distance between the anode and cathode was important for not only generating the arc, but also controlling the size of the SAC nanoparticles. When the distance between the anode and cathode is about 1 mm, nanoparticles with average size of 5–10 nm are produced. To examine the morphology and components of the SAC nanoparticles, a high-resolution TEM (JEM 100CX2) and X-ray diffraction (Bruker-AXS, New D8-Advance) were used. Also, DSC (TA Instrument Q20) with heating rate 10°C/min was used to obtain the endothermic peaks of the SAC nanoparticles. For the reflow test, we used a printed circuit board (PCB) made by a copper conductor, using electroless nickel immersion gold (ENIG) and a hot plate (NDK, NDK-1K) to maintain 170°C. The temperature was validated by T-type thermocouple. Finally, to obtain the thickness of the thin layer formed by the SAC nanoparticles, FIB (FEI, Helios Nano Lab 600) was used.

3. Results and discussion: As shown in Fig. 1, we observed that the nanoparticles were spherical in shape and that the size distribution varied mainly from 5 to 10 nm. Based on the

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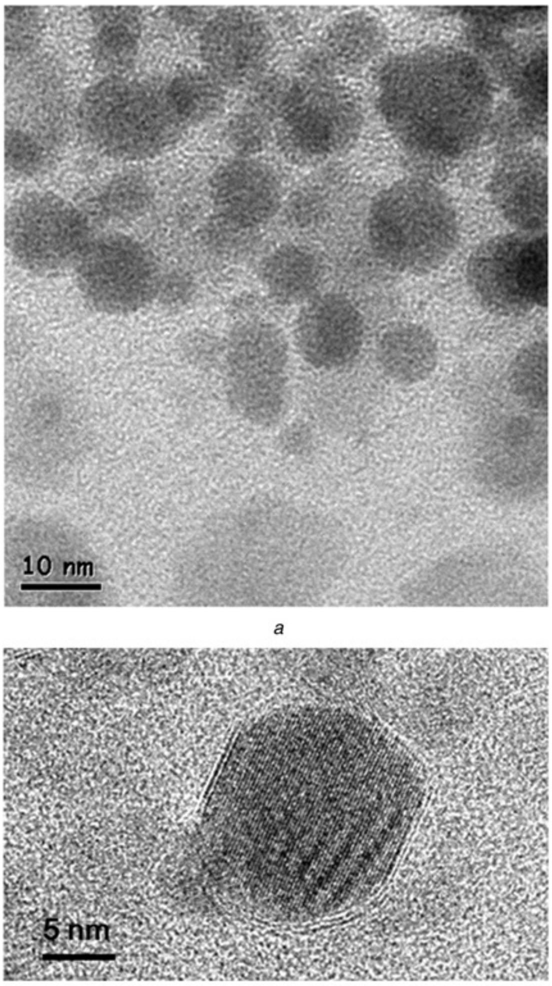

a

b

Fig. 1 *SAC particle size distribution and geometry of SAC nanoparticles manufactured by modified DCA method*
a Particle size distribution
b Geometry of SAC nanoparticles

measurement results of X-ray diffraction (XRD), we detected Sn, Ag, Cu phases in the nanoparticles, indicating that a good nanoparticle alloy was manufactured as shown in Fig. 2.

The measurement of the melting point of the SAC nanoparticles using DSC (TA Instrument, Q20) was continuously repeated twice without changing the sample. The measurement results are depicted in Fig. 3. The endothermic peaks were observed at 133, 162, and 218°C in the first cycle of the measurement.

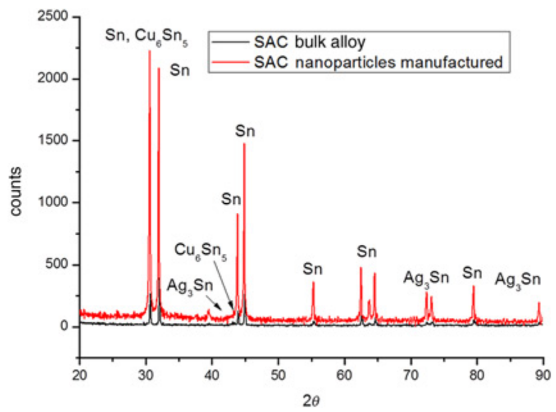

Fig. 2 *XRD results for SAC bulk alloy and SAC nanoparticles*

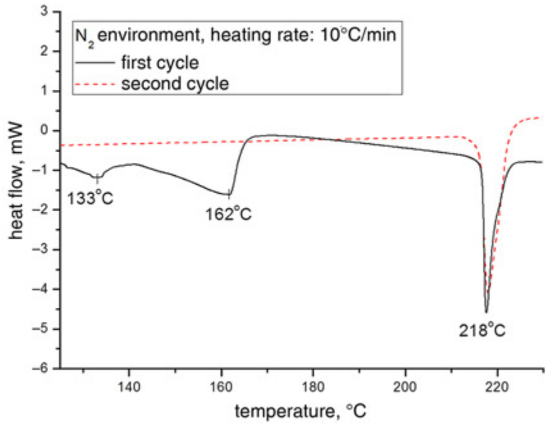

Fig. 3 *Endothermic peaks of the SAC nanoparticles measured by DSC (TA Instrument, Q20)*

The first and second peaks in the first cycle are broad due to the size distribution of SAC nanoparticles from 5 to 10 nm and also, as shown in Fig. 4, the peaks are well matched with a model presented by Hanszen [17] as given by

$$T_{\rm m} = T_o - \frac{2T_o}{\Delta H_o}\left[\frac{\sigma_{\rm s}}{\rho_{\rm s}(r-t_o)} + \left(\frac{\sigma_{\rm l}}{r} + \frac{\Delta P}{2}\right)\left(\frac{1}{\rho_{\rm s}} - \frac{1}{\rho_{\rm l}}\right)\right] \quad (1)$$

where $T_{\rm m}$, $T_o = 218^{\circ}$C are melting temperatures of nanoparticles and bulk materials of SAC, $\Delta H_o = 67$ J/g [10, 14] is bulk SAC's latent heat of fusion, $\sigma_{\rm s} = 0.082$ J/m^2 [10, 14] and $\sigma_{\rm l} = 0.43$ J/m^2 [10, 14] are the interfacial surface tensions between the solid and the liquid and between the liquid and its vapour, respectively. We used the assumption that the density of the solid is similar to that of liquid ($\rho_{\rm s} = \rho_{\rm l} = 7.39$ g/cm^3) [10, 14]. In the second cycle of the measurement, we found only one peak at 218°C without changing sample. The peak measured in the second cycle implies that the SAC nanoparticles were completely melted and changed into the bulk-sized SAC in the first cycle.

To observe the transformation of nanosized SAC into bulk-sized SAC during melting with large melting-point depression, we conducted the reflow test of the SAC nanoparticles suspended in benzyl alcohol including flux with a PCB and a hot plate as shown in Fig. 5*a*. We manufactured the PCB with a copper conductor, using ENIG. We heated a hot plate to maintain 170°C, which we checked by T-type thermocouple. Then we mounted the PCB with the suspension containing the SAC nanoparticles on the hot plate. We were the first to observe that SAC nanoparticles

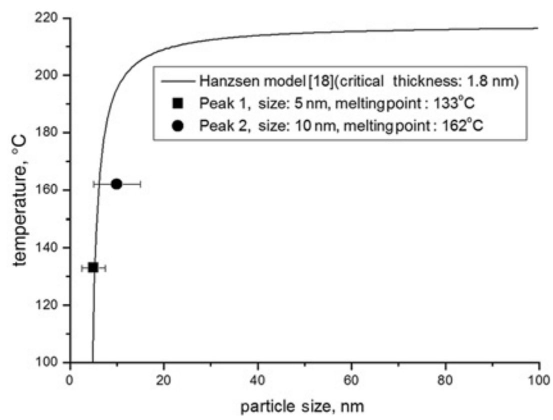

Fig. 4 *Comparisons of endothermic peaks measured by DSC in the first cycle with the Hanszen model [17]*

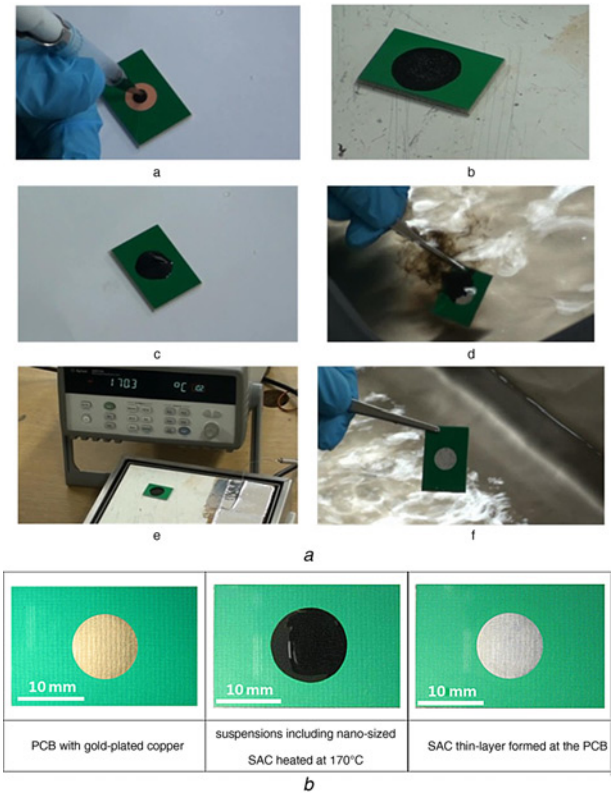

Fig. 5 *Experimental results for the reflow test at 170°C with SAC nanoparticles suspended in benzyl alcohol, using a PCB and a hot plate*
a Reflow test processes
b Reflow test results

were transformed to the bulk-sized SAC during the melting process at 170°C in less than 3 min as shown in Fig. 5*b*. Also, we observed the thin-layer geometry transformed from SAC nanoparticles after the melting process at the PCB.

Using a focused ion beam (FIB), we found that the thickness of the thin layer was, on average, 100 nm. The intermetallic compound Cu_6Sn_5 with 484.5 KeV as shown in Fig. 6 was detected between the SAC thin layer and a copper plate on the PCB using XPS. The presence of the intermetallic layer and the deposition of the copper plate showed that the complete melting phenomenon of SAC nanoparticles suspended in benzyl alcohol occurs at 170°C, which is 47°C lower than that of the SAC bulk material.

4. Conclusion: SAC nanoparticles were manufactured in dielectric benzyl alcohol, using the modified DCA method. The manufactured nanoparticles were spherical with size distribution mainly from 5 to 10 nm. Using DSC, we measured the endothermic peaks of the nanosized SAC with large melting-point depression and also compared the observed peaks with the theoretical model presented by Hanszen [17]. Based on the reflow test, we found that the SAC nanoparticles had been completely melted and changed into the bulk-sized SAC with a large melting-point depression (47°C). Also the results show that nanomaterials with nanoscale-properties can be converted into bulk-materials with bulk-properties during the reflow process.

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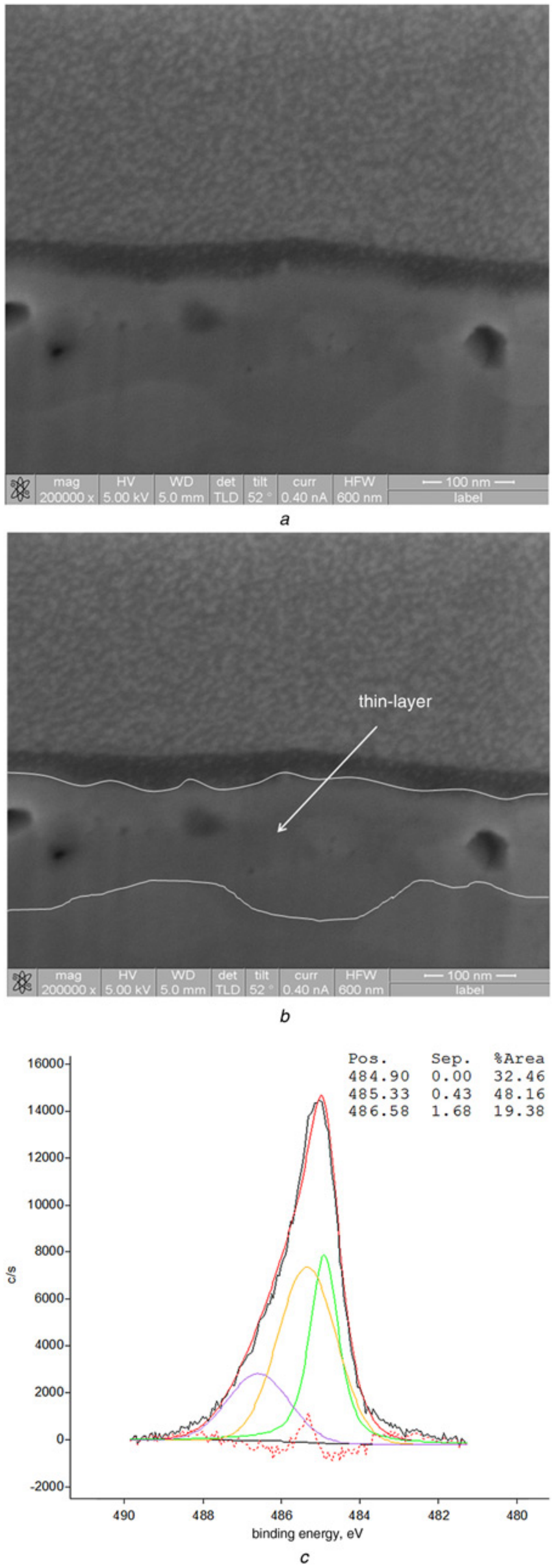

Fig. 6 *Thickness of the thin layer on PCB measured by FIB (focused ion beam) and the binding energy, 484 eV of intermetallic Cu_6Sn_5 between the SAC thin layer and a copper plate on PCB using XPS*
a Thickness of the thin layer (original image)
b Thickness of the thin layer (delineated image)
c Binding energy, 484 eV of intermetallic Cu_6Sn_5

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