

Sintering Characteristics of Micro-Zn Paste Containing Sn-3.0Ag-0.5Cu Nanoparticles

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Abstract. The transient liquid-phase sintering behavior of micro-Zn/nano-Sn-3.0Ag-0.5Cu (SAC) pastes was examined at a temperature of 190 °C as a function of the volume of ultrafine (~12.4 nm) SAC nanoparticles present. SAC nanoparticles have lower melting point drop than the bulk SAC particles. Although successful linkage at the interface between all Zn particles was not accomplished in all sintered samples, the number of linkages increased marginally with a decrease in the SAC content. As a result, the electrical resistivity of the sintered samples decreased with the decrease in the SAC content; however, the resistivities were still very high in all samples. Microstructural observations indicated that the observed results were mainly due to the short lifespan of the liquid phase caused by the coarsening of SAC nanoparticles during heating.

Introduction

A low-temperature, high-speed sintering process using an electrically conductive paste containing metal particles, which can be filled into the vias or through-holes in a substrate through screen printing, has long been demanded by the printed circuit board (PCB) industry [1,2]. This is because low-temperature sintering reduces warpage and thermal degradation in PCB fabrication. The high-speed sintering process using fill pastes can also enhance productivity and reduce energy consumption, in addition to suppressing thermal degradation.

In this study, the feasibility and characteristics of sintering a micro-Zn paste containing ultrafine Sn-3.0Ag-0.5Cu (wt%) (SAC) nanoparticles (NPs) were examined. The process of sintering of Zn/SAC pastes is represented schematically in Fig. 1. It was reported that a SAC NP melts at a lower temperature than a bulk SAC alloy (melting point: 217 °C) owing to the drop in melting points of NPs under ~30 nm in diameter due to Gibbs-Thomson effect [3,4]. In addition, the melting point of a SAC NP decreases more drastically as the diameter of the NP decreases to <20 nm [3,4]. Thus, if ultrafine SAC NPs are added between micron-sized Zn powders, a conductive network could be formed between the Zn powders at a relatively low temperature; this temperature is dependent on the size of the NPs. In other words, the SAC NPs would play the role of a metal binder at a relatively low temperature. Melting of the NPs cannot continue for a long time, as coarse NPs with relatively high melting points are formed by the agglomeration of ultrafine NPs. Therefore, this process can be designated as transient liquid-phase sintering (TLPS). In our study, micron-sized Zn powder was used as the main conductive filler because of its excellent electrical and thermal properties and low raw material cost. The main process parameter considered was the volume of the added SAC NPs.

Experimental

The Zn powder used was purchased from Kojundo Chemical Laboratory Co., Ltd. The diameter of the Zn powders ranged from 1 to 15 μm, and the average diameter was ~3 μm. A scanning electron microscopy (SEM) image of the Zn powders is presented in Fig. 2(a). The SAC NPs were fabricated in-house. The surface of the SAC NPs was not contaminated with any capping material or surface stabilizer, and the oxidation was also minimized. The diameter of the SAC NPs ranged from 2.3 to 37.6 nm, and the average diameter was ~12.4 nm (Fig. 2b). The SAC NPs were prepared in solution state.

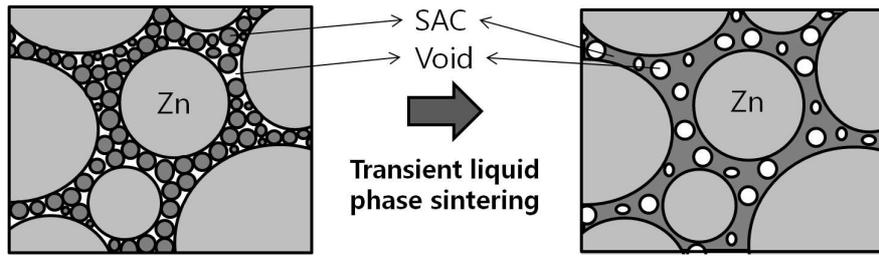
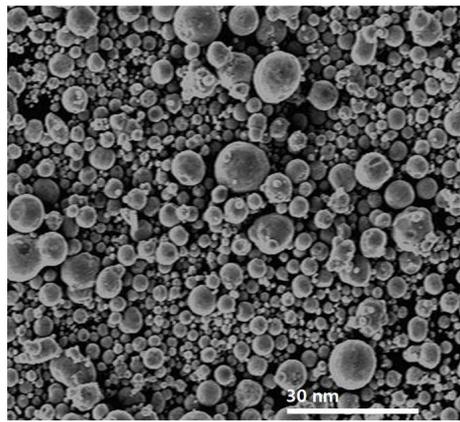


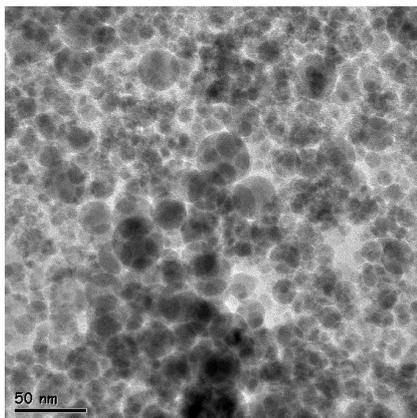
Fig. 1. Schematic representation of sintering of micro-Zn/ultrafine nano-SAC paste.

The Zn/SAC paste was produced as follows. Zn powder was added to a solution containing SAC NPs, and the excess solvent was removed in a low-vacuum chamber maintained at 60 °C. Then, the remnant was mixed with a commercial soldering flux (water flux: #1, Indium Corporation of America), adopted for soldering Zn, using a homogenizer (Pro-200, Pro Scientific Inc.). The amount of flux added was 10% of the total weight of the Zn powders and SAC NPs.

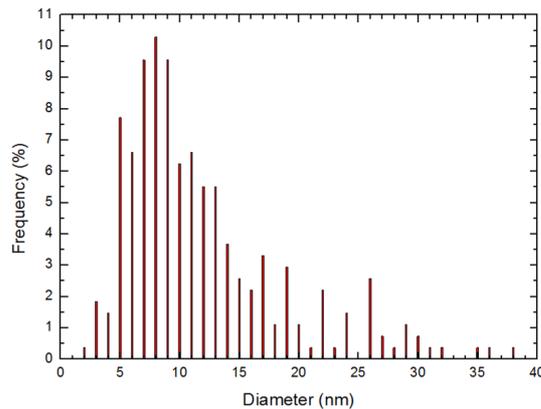
The produced Zn/SAC paste was filled into through-holes in PCBs by screen printing and then sintered for 15 min at 190 °C. The microstructure along the cross section of the sintered PCB was observed using SEM (S-2700, Hitachi Ltd.). The electrical resistivity of the sintered samples was also measured along the cross section using two probes set at ~1 mm interval. The microstructures and electrical resistivity were analyzed as functions of the volume of SAC NPs added.



(a)



(b)



(c)

Fig. 2. (a) SEM image of Zn powders, and (b) TEM image and (c) size distribution of SAC NPs used in this study.

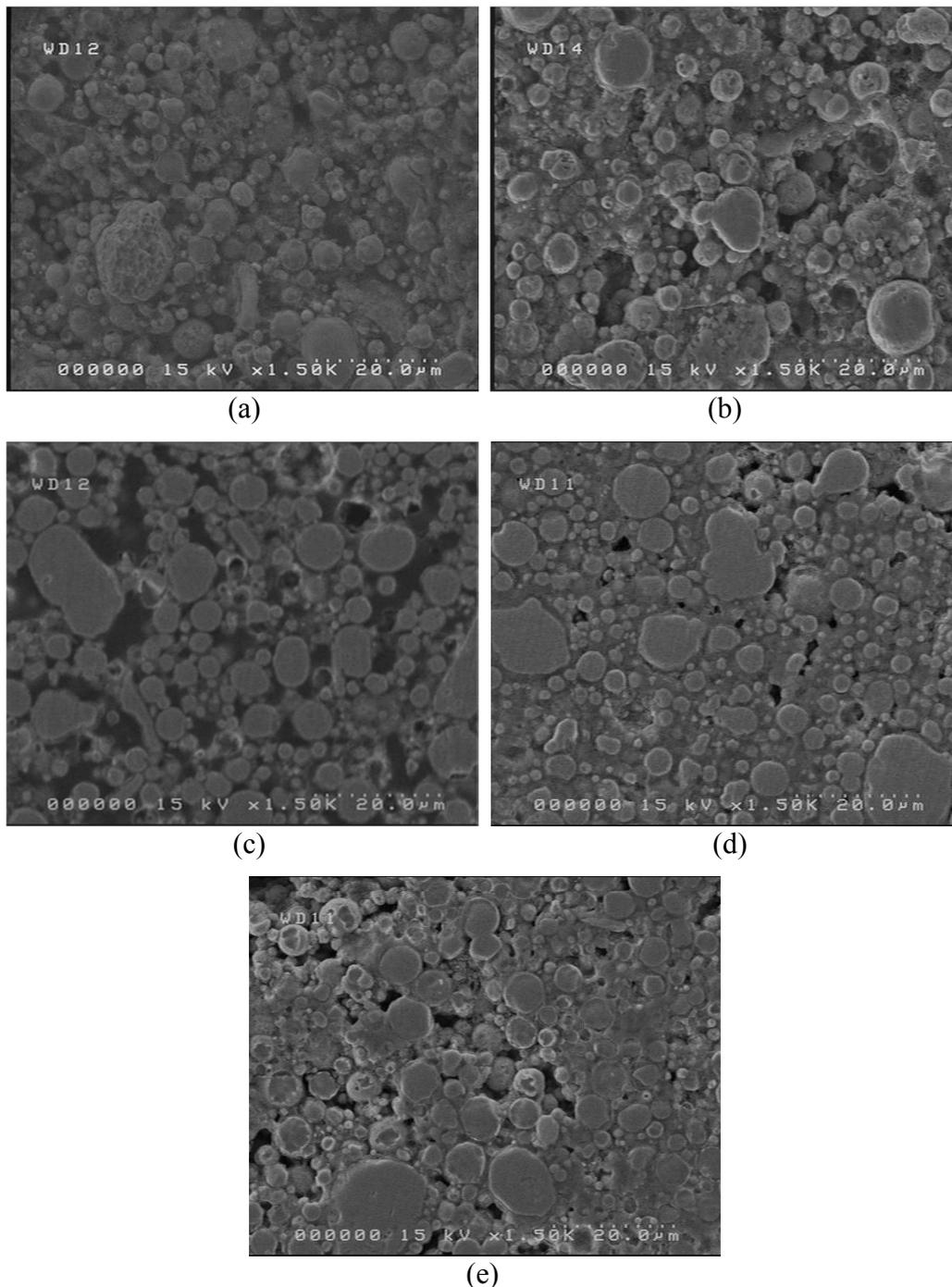


Fig. 3. SEM images of samples sintered at a low temperature of 190 °C as functions of the amount of SAC NPs present: (a) 27 vol%, (b) 25 vol%, (c) 22 vol%, (d) 10 vol%, and (e) 7 vol%.

Results and Discussion

Fig. 3 shows the microstructures of the sintered samples as functions of the the volume of SAC NPs added. The samples were sintered at a temperature of 190 °C, which is lower than the melting point of the bulk SAC alloy. Although a completely linked microstructure was not found in all sintered samples, the degree of linkage increased marginally as the amount of SAC NPs decreased. This result implies that the TLPS achieved through melting of SAC NPs proceeds effectively when the amount of SAC NP is low. As shown in Fig. 3(a)–(c), the samples having SAC NPs in excess of 20 vol% were fragile. The structural linkages between the Zn particles were few in this case, meaning that TLPS was insignificant. In contrast, for samples with less than 10 vol% SAC NPs, the structural linkages made of SAC were observed at intervals in the samples as shown in Fig. 3(d)–(e). A detailed image of the linked structure observed in sintered Zn/SAC specimen containing 7 vol% SAC NPs is shown in

Fig. 4. It was observed that all the spaces between the Zn particles were filled with the flux residue, a non-conducting organic compound derived from the flux material, regardless of whether the Zn particles were linked with SAC alloy or not. As a result, it was concluded that the addition of SAC NPs in low quantity is advantageous in achieving the desired microstructure by TLPS. The reason for and case studies on this behavior are discussed in the following section.

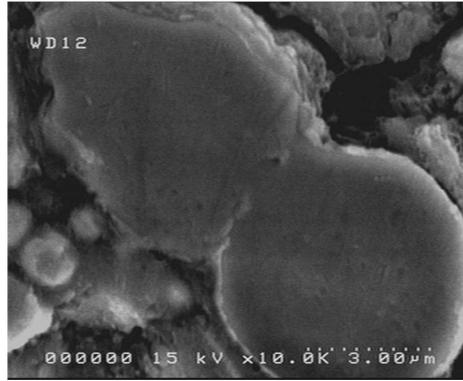


Fig. 4. SEM image showing the linkage between Zn particles in a sintered specimen with 7 vol% SAC NPs.

The electrical resistivities of the samples measured as a function of the SAC content are presented in Table 1. Even if the electrical resistivities were very high in all samples, the resistivity decreased with a decrease in the SAC content, identical to the microstructural behavior.

Table 1. Summary of electrical resistivities measured in each sample.

Paste sample #	#1	#2	#3	#4	#5
Amount of SAC nanoparticles (vol%)	27	25	22	10	7
Electrical resistivity (M Ω)	19,000	3,100	1,500	800	200

Fig. 5 shows the backscattered electron image (BEI) and electron probe microanalyzer (EPMA) map of the specimen sintered using the #2 paste. Irregularly shaped Sn, a major component of the SAC, was widely distributed along the contours of the Zn particles; however, the distribution was irregular. However, this may be because a large part of the ultrafine SAC phase may go undetected at the resolution employed. SAC phases having diameters of up to several hundred nanometers or even several micrometers were observed. The grown SAC phases failed to form the series of linkages required to obtain sufficiently high conductivity in composite structures and thereby resulted in the observed high electrical resistivities.

The growth of SAC phases is caused by the coarsening of the melted SAC NPs. However, the diameter of the SAC phases should not exceed ~ 13 nm, so that the melting point of the SAC phases is still maintained at a temperature lower than the sintering temperature of 190 °C [3,4]. The grown SAC phases having diameters >13 nm will instantly solidify because the sintering temperature is lower than the melting point of the grown phases. The solid SAC phases in this case may not bind immediately with the Zn particles, and therefore, the SAC phases can undergo neck formation only via solid-phase sintering at 190 °C. However, the solid SAC phases may not be sintered along with the Zn particles to the stage of neck formation within the short sintering time of 15 min. Moreover, the spaces existing among the solid SAC phases and the Zn particles can be a serious impediment to rapid solid-phase sintering. Similar results can be observed for some of the added SAC NPs whose initial diameters were larger than ~ 13 nm.

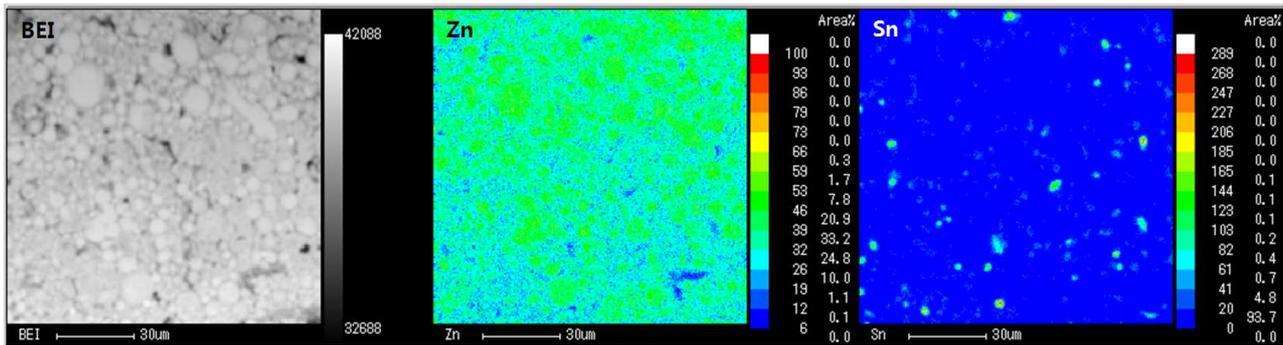


Fig. 5. BEI and EPMA map of sintered specimen of Zn/25 vol% SAC paste.

In summary, SAC NPs should wet the micro-Zn particles or agglomerate with other SAC NPs during sintering at temperatures higher than the low melting point of SAC NPs. Therefore, SAC NPs immediately solidify after melting, and this leads to transient melting during reflow of ultrafine SAC NPs.

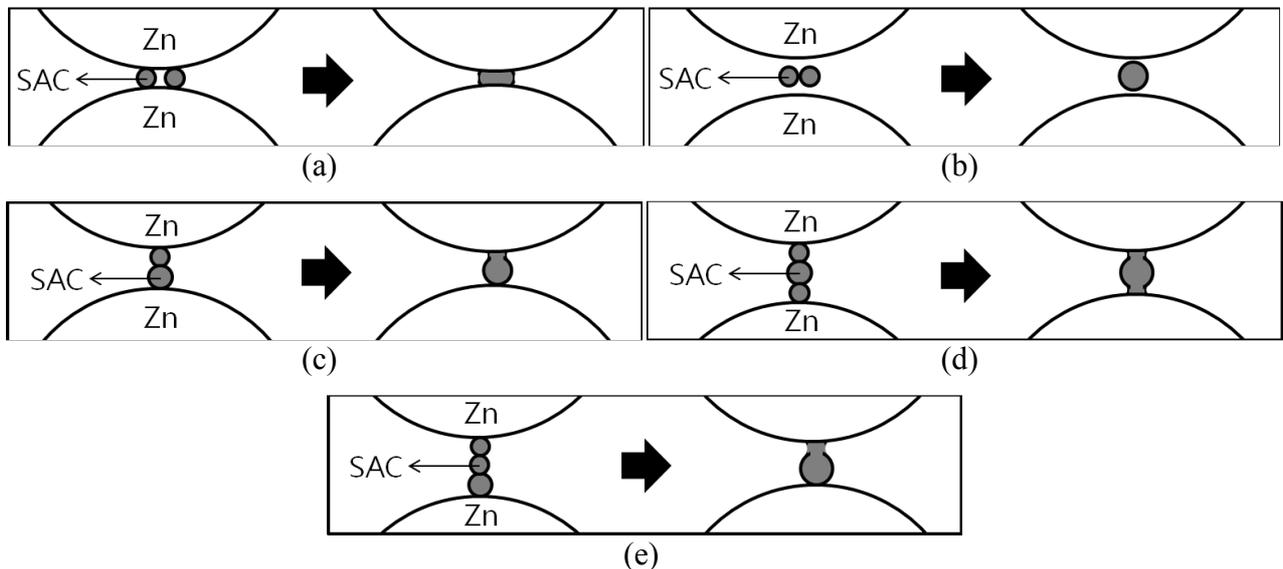


Fig. 6. Schematics of case study on the transient liquid-phase sintering characteristics of micro-Zn/ultrafine nano-SAC paste. The order of appearance of the particles in the vertical direction is (a) micro-Zn/nano-SAC/micro-Zn, (b) micro-Zn/space/nano-SAC/space/micro-Zn, (c) micro-Zn/small-nano-SAC/large-nano-SAC/micro-Zn, (d) micro-Zn/small-nano-SAC/large-nano-SAC/small-nano-SAC/micro-Zn, and (e) micro-Zn/small nano-SAC/small-nano-SAC/large-nano-SAC/micro-Zn.

Fig. 6 shows the schematics explaining the case study on the TLPS characteristics of a micro-Zn/ultrafine nano-SAC paste. When SAC NPs having melting points of $<190\text{ }^{\circ}\text{C}$ occur between the micro-Zn particles (Fig. 6a), the Zn particles can be linked physically and electrically by the melting of and wetting by NPs during sintering. However, if a space occurs between the micro-Zn particles and the SAC NPs, the linkage cannot be established at low temperatures. This is because of the coarsening of NPs due to agglomeration, when not in contact with the Zn particles (Fig. 6b). In the case where SAC NPs line up vertically, more detailed discussion is needed. When a small and a large SAC NP are vertically stacked between two micro-Zn particles (Fig. 6c, it should be noted that the size of the neighboring NPs always differs), the large-SAC-NP/Zn-particle interface cannot be linked, whereas the small-SAC-NP/Zn-particle interfaces can be linked. Thus, an effective electrical path cannot be made in this case. In the case where SAC NPs line up vertically in the order of small/large/small NP (Fig. 6d), the four interfaces can be linked successfully. However, the four interfaces cannot be linked when the large NP is in contact with the Zn particle (Fig. 6e), which corresponds to the majority of the cases. On the basis of similar reasoning, we postulate that the

probability of the formation of complete linkage would be extremely low in the cases where more than four SAC NPs line up vertically. In other words, the formation of a complete linkage in any case is possible only when the arrangement of particles is regular in the sequence of Zn particle/small NP/large NP/small NP/.../small NP/Zn particle. Thus, this hypothesis accounts for the increase in electrical resistivity with the increase in the amount of SAC NPs added.

Summary

In order to facilitate low-temperature and high-speed sintering using low melting point of ultrafine SAC NPs, the feasibility and characteristics of sintering micro-Zn/nano-SAC pastes were examined as a function of the volume of SAC NPs added. Although a completely linked microstructure was not found in all samples sintered at 190 °C, which is lower than the melting temperature of the bulk SAC alloy by 27 °C, the degree of linkage increased marginally with the decrease in the amount of SAC NPs. Similarly, the resistivity also decreased with the decrease in the amount of SAC NPs; however, the electrical resistivities were still very high in all sintered samples. Through a detailed microstructural study, it was postulated that the results observed were mainly due to the short lifespan of the liquid phase caused by the coarsening of SAC NPs during sintering.

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References

- [1] S.K. Kang, S.L. Buchwalter, N.C. LaBianca, J. Gelorme, S. Purushothaman, K. Papatomas, M. Poloks, Development of conductive adhesive materials for via fill applications, *IEEE Trans. Compon. Packag. Technol.* 24(3) (2001) 431-435.
- [2] Y.-S Eom, K.-S. Choi, S.-H Moon, J.-H. Park, J.-H. Lee, J.-T. Moon, Characterization of a hybrid Cu paste as an isotropic conductive adhesive, *ETRI J.* 33(6) (2011) 864-870.
- [3] C.D. Zou, Y.L. Gao, B. Yang, X.Z. Xia, Q.J. Zhai, C. Andersson, J. Liu, Nanoparticles of the lead-free solder alloy Sn-3.0Ag-0.5Cu with large melting temperature depression, 38(2) (2009) 351-355.
- [4] Y. Gao, C. Zou, B. Yang, Q. Zhai, J. Liu, E. Zhuravlev, C. Schick, Nanoparticles of SnAgCu lead-free solder alloy with an equivalent melting temperature of SnPb solder alloy, *J. Alloys Compd.* 484 (2009) 777-781.

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