

## DEVELOPMENT OF HEAT RESISTANT Pb-FREE JOINTS BY TLPS PROCESS OF Ag AND Sn-Bi-Ag ALLOY POWDERS

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### Abstract

TLPS (Transient Liquid Phase Sintering) process is a candidate method for heat-resistant bonding, which makes use of the reaction between low-melting temperature powder of Sn-Bi base alloys and reactive powder of Ag. During heat treatment above the melting temperature of a Sn-Bi base alloy, the molten Sn-Bi reacts rapidly with solid Ag particles, which results in the formation of a heat-resistant intermetallic compound (IMC). In this study, the TLPS properties between Sn-17Bi-1Ag (at.%) powder with a liquidus temperature of 200°C and pure Ag powder were investigated. During differential scanning calorimetry (DSC) measurement, an exothermic reaction and an endothermic reaction occurred, which correspond to the formation of the  $\epsilon$ -Ag<sub>3</sub>Sn-IMC phase and the melting of the Sn-17Bi-1Ag alloy, respectively. After the overall measurement, the obtained reactant consisted of the Ag<sub>3</sub>Sn-IMC and Bi-rich phases, both of which started melting above 250°C, with a small amount of the residual Sn-Bi eutectic phase. These results suggest that the TLPS process can be applied for Pb-free heat-resistant bonding.

**Keywords:** Transient Liquid Phase Sintering (TLPS), CALPHAD, High-temperature Pb-free solder

### 1. Introduction

High-temperature Pb-free solders able to withstand temperatures beyond 250°C and with soldering temperatures as low as possible, for instance around the melting temperature ( $T_m$ ) of Sn-base Pb-free solders around 220°C, are required for electronic packaging industries. The adhesion method using organo-metallic Ag nano-particles applied for joining electronic components on a Cu substrate is one of the candidate techniques, in which bonding conditions are satisfied at relatively low temperatures at around 300°C with loading pressure of 1 to 5 MPa [1,2]. It has also been found that heat-resistance of jointed assemblies is achieved at a melting temperature of Ag of 961°C. Its bonding procedure occurs due to a surface energy effect caused by nano-sized Ag particles with a large amount of surface area. However, this method would be impractical because of the high cost of Ag nano-particles as well as requirement of high pressure condition.

On the other hand, Corbin *et al.* reported the possibility of transient liquid phase sintering (TLPS) process applied for low-temperature bonding with heat resistance, in which powder of low- $T_m$  materials, such as pure Sn, eutectic Sn-Pb and Sn-Bi alloys, and reactant powder of Cu are mixed and heat-treated above each  $T_m$  [3-6]. During the TLPS process conducted

above  $T_m$  of the low- $T_m$  powder, a liquid phase appears and enhances the reaction with reactant powder, which results in the formation of high- $T_m$  intermetallic compound (IMC) phases with consumption of the low- $T_m$  substance. In the case of TLPS between eutectic Sn-Bi and pure Cu powders studied by differential scanning calorimetry (DSC), the Sn-Bi powder starts melting above 139°C and then reacts with Cu particles to form Sn-Cu IMC phases, such as Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub>, as well as Bi-rich particles eliminated from the Sn-Bi powder, both of which exhibited high  $T_m$  above 270°C. As a result, heat-resistance of a solder joint can be achieved. In the case of TLPS of a Cu-45Sn-5Bi (mass%) mixture consisting of pure Cu (50mass%), pure Sn (41.5%) and eutectic Sn-Bi (8.5%) powders, the eutectic Sn-Bi phase has been found to remain after the reaction [6], which suggests that conditions of mixing and heat treatment should be optimized for low-temperature bonding of heat-resistant solders.

In the present study, reactions between gas-atomized powders of Sn-17Bi-1Ag (at.%) alloy and pure Ag during the TLPS were investigated. Ag was chosen as a reactant powder because Ag has superior oxidation resistance as well as high reactivity with Sn as compared with Cu [7]. Ag-Sn IMC and Bi solution phases, both of which have heat-resistance above 270°C, are expected to form as reaction products after the TLPS.

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## 2. Experimental Procedure

The characteristics of the prepared powders are listed in Table 1. Each powder consisted of spherical particles of a raw material produced by gas-atomize process. Multi-step sieves with mesh grids of 53-, 25-, 20- and 5- $\mu\text{m}$  square were used to screen Ag powder. Powders out of the range of 5- to 53- $\mu\text{m}$  square were not used for experiment because their quantity is quite small. Ag powders were classified into three groups, i.e., fine (5-20 $\mu\text{m}$ ), medium (20-25 $\mu\text{m}$ ), and coarse (25-53 $\mu\text{m}$ ) grades, to investigate the effect of Ag particle size on the TLPS process. Appropriate amounts of Ag and Sn-17Bi-1Ag alloy powders were mixed in a mortar to prepare samples denoted as #1 and #2, the blending quantities and entire chemical compositions of which are listed in Table 2. Under a pressure of 9.8 MPa, mixed powders were into disks of 5mm in diameter. Both thermal analysis and TLPS heat treatment of the disks were carried out simultaneously by DSC (Netzsch DSC 404C) under an argon gas flow. Samples were heated up to  $T_{\text{max}}$  ( $T_{\text{max}} = 250, 280$  and  $300$  °C) at heating rate of  $5$  °C/min and then maintained at  $T_{\text{max}}$  for 10 or 60 min, followed by cooling down to room temperature (RT) at a cooling rate of  $-5$ °C/min. Thermal analysis, heating up to  $300$ °C at a rate of  $5$ °C/min, holding at  $300$ °C for 10 min, and cooling down to RT at a rate of  $-5$ °C/min, was performed again on the TLPS-treated samples to confirm that the reactions occurred during TLPS. To examine the effects of Ag particle size on the TLPS reactions, samples of #1x (x=F, M, C) and #2x (x=F, M, C) were prepared by blending Sn-17Bi-1Ag powder with fine (F), medium (M) and coarse (C) Ag powders, experiments the same as the above

**Table 1.** Characteristics of Ag and Sn-Bi-Ag alloy powders applied in the TLPS process.

Powder	Diameter /mm	Chemical composition /at.%	Melting temperature /°C
Fine Ag	maj-20	99.99 Ag	961.9
Medium Ag	20 - 25		
Coarse Ag	25 - 53		
Sn-17Bi-1Ag	< 53	82Sn-17Bi-1Ag	140 / 200

**Table 2.** Blend ratio and substantial composition of TLPS samples.

Sample	Blend ratio /g		Substantial chemical composition /at.%			
	Ag	Sn-17Bi-1Ag	Ag	Sn	Bi	Ag/Sn
#1	0.137	0.063	74	22	4	3.36
#2	0.134	0.066	71	24	5	2.96

were performed.

Microstructure examination and composition analysis were carried out by an electron probe micro-analyzer (EPMA, JEOL JXA-8100) with an accelerating voltage of 20 kV and a probe current of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-8}$  A. The volume fraction of void in each sample was determined by averaging 5 measured values by an image analysis software (WinROOF). Chemical compositions of the phases which appeared were determined by the EPMA with the ZAF calibration method using standard samples of pure Ag, Sn and Bi.

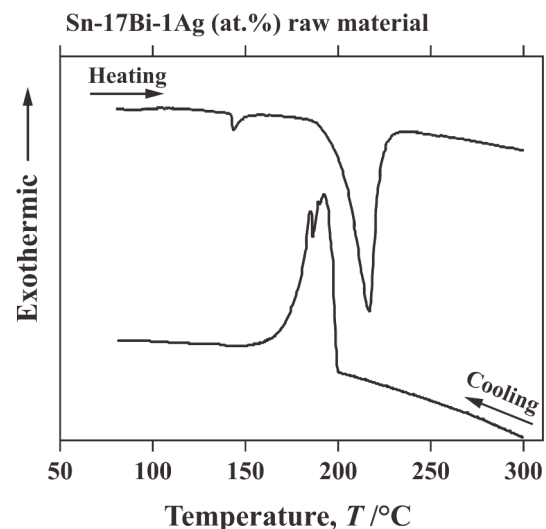
## 3. Results & Discussion

### 3.1 Thermal analysis of Sn-17Bi-1Ag raw material powder

Figure 1 shows DSC curves of the Sn-17Bi-1Ag raw material powder. In the heating curve, a small endothermic signal was detected at about  $140$ °C, which corresponds to the eutectic reaction of the Sn-Bi binary system. A large endothermic signal starting at about  $180$ °C and terminating at  $220$ °C corresponds to the solidus and liquidus temperatures, respectively. In the cooling curve, a large exothermic signal rising at  $200$ °C corresponds to the beginning of solidification. This disagreement with the liquidus temperature at  $220$ °C is caused by the super-cooling effect.

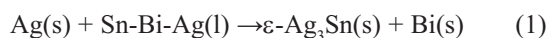
### 3.2 Thermal analysis and microstructure examination of #1x (x=F, M, C) samples

Figure 2 shows DSC curves of blended samples, #1F, #1M and #1C. All the heating curves seem to be similar as shown in Fig.2(a). However, exothermic



**Figure 1.** Result of DSC measurement of Sn-17Bi-1Ag (at.%) alloy.

deviation from the baseline starts rising at 143°C (#1F), 153°C (#1M) and 163°C (#1C), which suggests that the reaction between Ag and Sn-17Bi-1Ag powders to form the  $\epsilon$ -Ag<sub>3</sub>Sn phase is enhanced with decreasing size of Ag powder. An endothermic reaction appeared between 180 and 220°C, which forms a valley in a mountain of the exothermic reaction, corresponds to the melting reaction of Sn-17Bi-1Ag alloy. At the same time, the formation of the  $\epsilon$ -Ag<sub>3</sub>Sn continues to proceed with the release of formation enthalpy of the  $\epsilon$ -Ag<sub>3</sub>Sn due to the following reaction:



where (s) and (l) represent solid and liquid, respectively. If the blending quantity of Ag and Sn-17Bi-1Ag powders is appropriate, the reaction products are  $\epsilon$ -Ag<sub>3</sub>Sn(s) and Bi(s), which would not melt up to the  $T_m$  of Bi, 270°C. The effects of Ag size is clearly seen in the cooling curves of #1F, #1M and #1C as shown in Fig.2(b). A sharp exothermic signal which appears at 240°C in the curve of #1F is caused by the latent heat of Bi-rich liquid with the under cooling effect. No other signal appeared after the

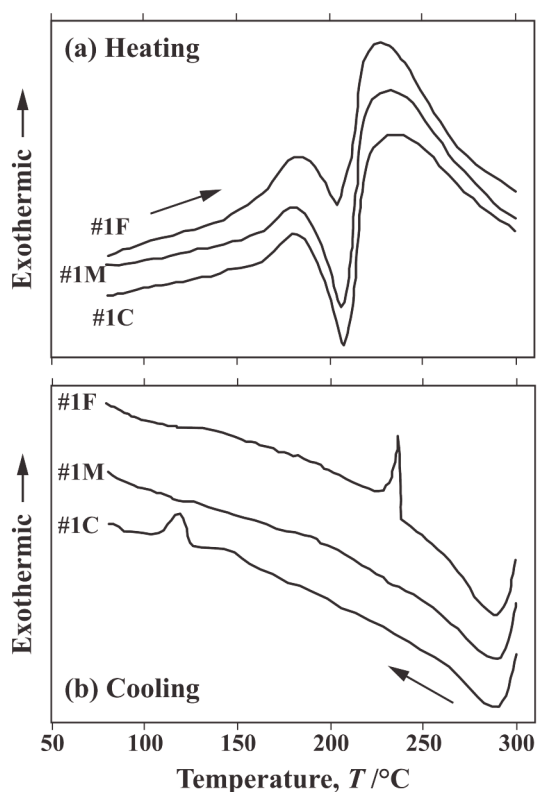
solidification of the Bi-rich liquid was terminated. Therefore, Sn contained in the Sn-17Bi-1Ag powder was completely consumed by fine Ag particles in sample #1F. On the other hand in the curve of #1C, an exothermic signal starts rising at 125°C, which seems to correspond to the super-cooled eutectic point of Sn-Bi alloy at 139°C. This suggests that a considerable amount of the low  $T_m$  phase" of Sn-Bi alloy remains at temperatures above 125°C, which might deteriorate the heat resistance of the TLPS treated solders.

Figure 3 shows backscattered electron (BSE) images of the TLPS-treated samples of #1F, #1M and #1C. In all the images, black areas represent residual voids. Gray, dark gray and white areas correspond to the  $\epsilon$ -Ag<sub>3</sub>Sn, (Ag) and (Bi) phases, respectively, according to the composition analysis by EPMA. Only in the #1C sample, relatively bright gray particles of (Sn) were observed around (Bi) particles, which caused the eutectic reaction of the Sn-Bi alloy. In the low magnified images, the outline of the original Ag particles can be distinguished by chained voids, which is consistent with the classification of #1F (5-20 $\mu$ m), #1M (20-25 $\mu$ m), and #1C (25-53 $\mu$ m). In the latter two samples, unreacting Ag remains like the yolk of an egg. The thickness of the white, i.e., the  $\epsilon$ -Ag<sub>3</sub>Sn phase around Ag yolk, is approximately 10  $\mu$ m, which indicates that all of the Ag particles below 20 $\mu$ m in diameter react with Sn to form  $\epsilon$ -Ag<sub>3</sub>Sn. That is the reason why all of the Sn in the Sn-17Bi-1Ag powder was consumed during the TLPS of the #1F (5-20 $\mu$ m) sample.

In addition to the reactivity between the Ag particles and the Sn in the Sn-17Bi-1Ag powder, fineness of the Ag particles is an advantage for reducing the formation of voids. According to the microstructures shown in Fig. 3, the volume fraction of voids was measured to be 7.5%, 19% and 19% in #1F, #1M and #1C samples, respectively, which suggested that the fine Ag particles should be chosen in the following experiments.

### 3.3 Effect of maximum temperature, $T_{max}$ , and holding time, $t_h$ , on TLPS process

DSC measurement during various heating conditions of the TLPS process was performed on #1F blended samples to investigate the effects of  $T_{max}$  and  $t_h$ . Obtained cooling curves are shown in Fig. 4. Two kinds of exothermic signals at about 140°C and 240°C were detected. The former seems to correspond to the eutectic reaction of the Sn-Bi system and the latter to the super-cooled eutectic reaction in the Bi-Ag system. The lower  $T_{max}$  of 250°C and 280°C as well as shorter  $t_h$  of 10min resulted in the formation of the residual Sn due to insufficient reaction with fine Ag particles. Under the other conditions, only a high temperature signal at about 240°C was obtained. To prevent the eutectic reaction of



**Figure 2.** Result of DSC measurement of blended samples of Sn-17Bi-1Ag (at.%) and Ag powders. #1 represents the blend ratio shown in Table 2. F, M and C represent the size of Ag particles, fine, medium and coarse, respectively, shown in Table 1.



the Sn-Bi system at 140°C for high-temperature resistance,  $T_{max}$  and  $t_h$  should be optimized.

### 3.4 Effect of blend ratio of Ag and Sn-17Bi-1Ag powders

The blend ratio of Ag and Sn-17Bi-1Ag powders as well as the heating condition was optimized based on the phase diagram shown in Fig. 5 calculated by Pandat [8] with thermodynamic database ADAMIS [9,10]. The calculation was performed along Ag to

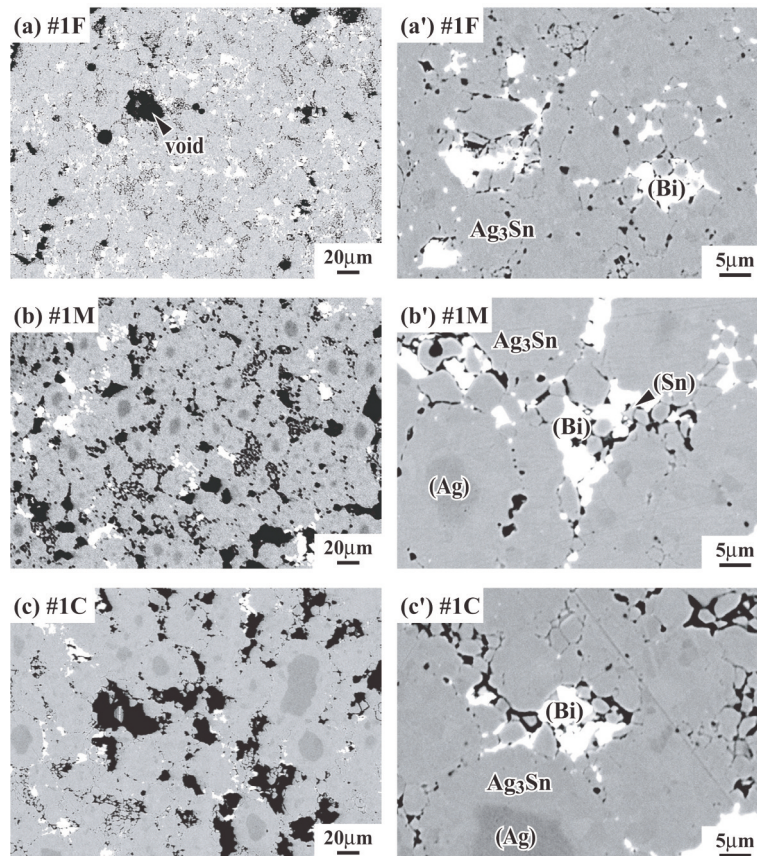


Figure 3. BSE images of microstructure of #1F, #1M and #1C samples after the TLPS process under the condition of  $T_{max} = 300^\circ\text{C}$  and  $t_h = 10\text{min}$ .

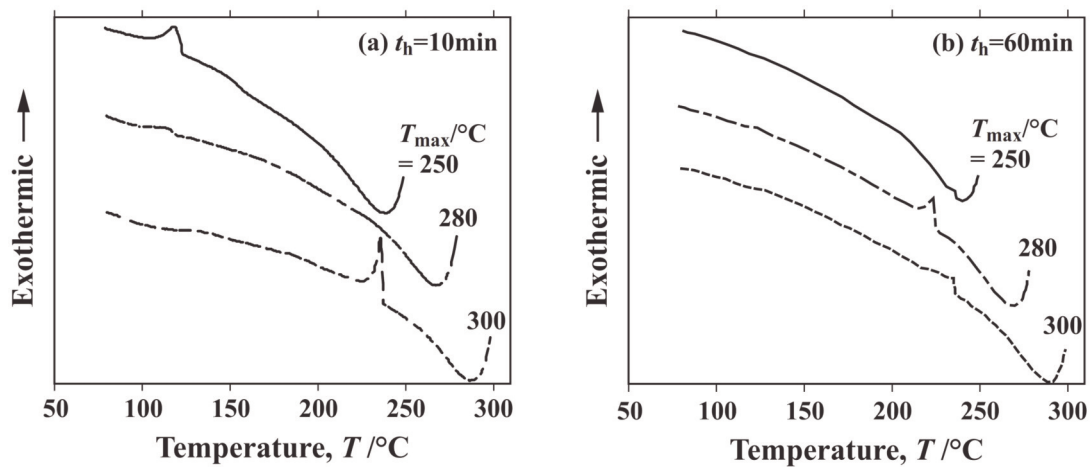
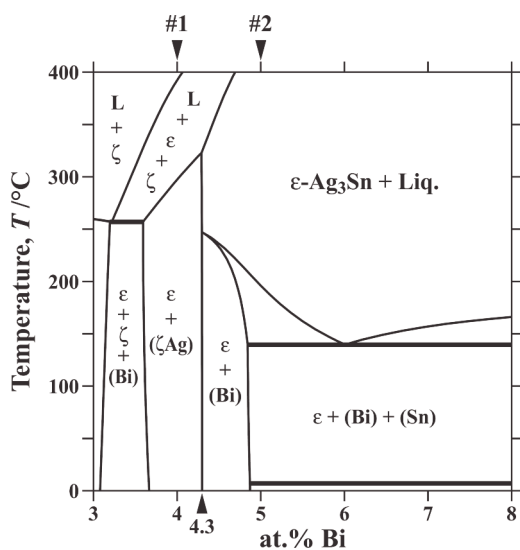


Figure 4. Result of DSC measurement of blended #1 samples. Conditions of the TLPS process were (a)  $T_{max} = 250, 280$  and  $300^\circ\text{C}$  and  $t_h = 10\text{min}$ . and (b)  $T_{max} = 250, 280$  and  $300^\circ\text{C}$  and  $t_h = 60\text{min}$ .



**Figure 5.** Phase diagram calculated along pure Ag to Sn-17Bi-1Ag (at.%) in the substantial Bi composition between 3 and 8 at.%.

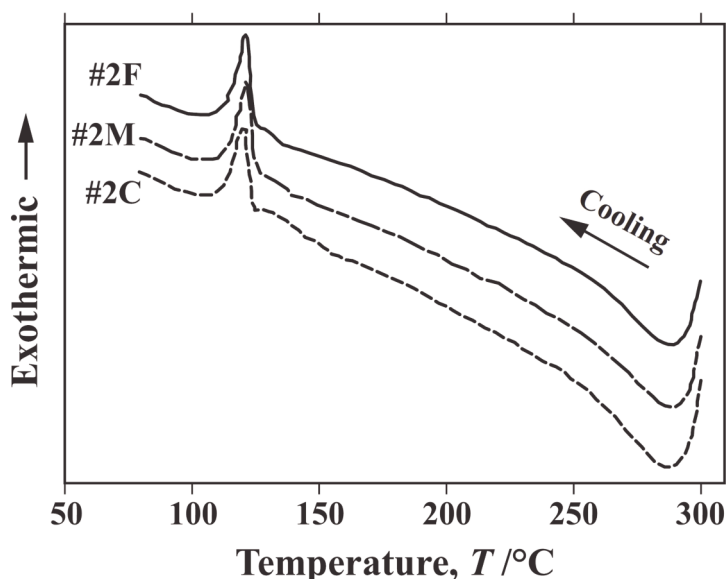
Sn-17Bi-1Ag section and the content of Bi was chosen as the abscissa. The blend ratios shown in Table 2 are drawn as #1 and #2 in the phase diagram. According to the calculated phase diagram, it can be assumed that the solidification terminates by invariant reactions:  $L + (\zeta\text{Ag}) = \epsilon + (\text{Bi})$  at 256.8°C below 4.3at.% Bi, and  $L + \epsilon\text{-Ag}_3\text{Sn} = (\text{Bi}) + (\text{Sn})$  at 139.5°C above 4.3at.% Bi. Therefore, if the reaction between Ag and Sn-17Bi-1Ag powders was completed thoroughly, the DSC signals due to the invariant reactions appeared at 256.8°C in the #1 sample, and at

139.5°C in the #2 sample. Insufficient reaction with some amount of residual Ag caused the increase of substantial Bi content in the reacted portions, which reasonably explains the low-temperature signals of DSC at about 140°C appeared in the #1C sample in Fig.2(b) and in the #1F samples in Fig. 4(a). Figure 6 shows DSC curves measured for #2 powders mixed with fine (#2F), middle (#2M) and coarse (#2C) Ag, whose substantial chemical composition is Ag-24Sn-5Bi (at.%). Obtained microstructures after the DSC measurement are shown in Fig. 7. Even in the case of the fine Ag sample (#2F) without residual Ag phase shown in Fig. 7(b), the low-temperature signal due to the  $L + \epsilon\text{-Ag}_3\text{Sn} = (\text{Bi}) + (\text{Sn})$  invariant reaction appears, which suggests that excessive solder powder causes the formation of low-temperature melt of Sn and Bi. In summary, the blend ratio of Ag and Sn-17Bi-1Ag powders should be less than 4.3at.% in the substantial chemical composition of Bi.

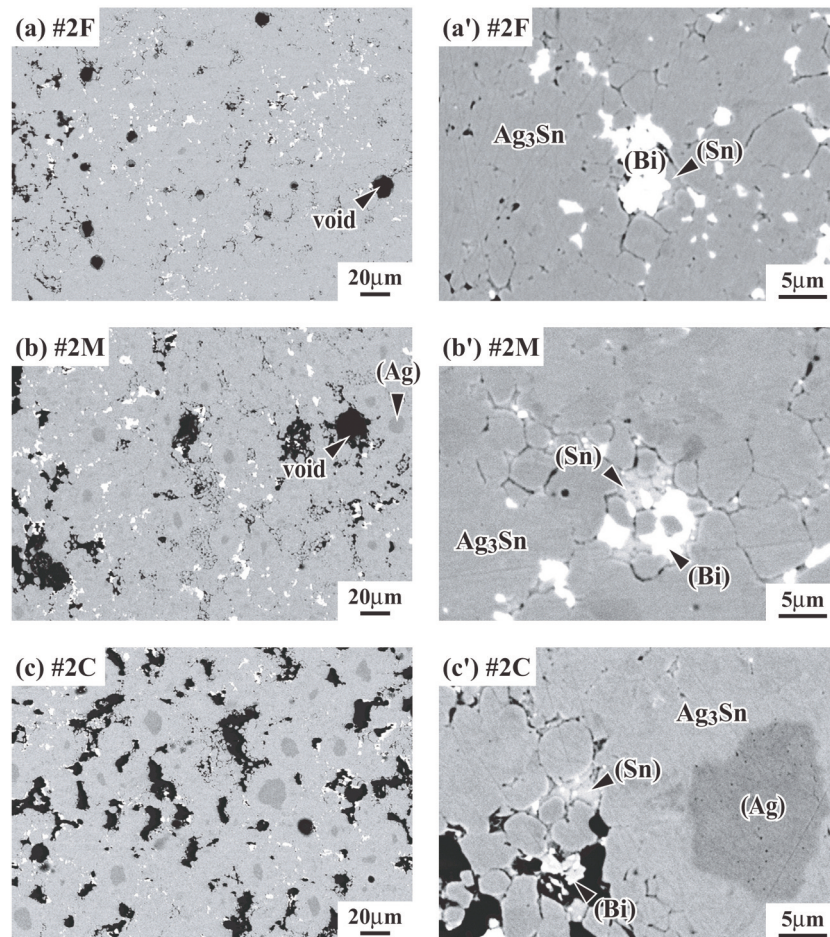
#### 4. Conclusions

The possibility of the The TLPS (Transient Liquid Phase Sintering) process using blended powders of Ag and Sn-17Bi-1Ag alloy for heat-resistant soldering was evaluated by microstructure examination and DSC measurement as a simulation of the TLPS process. Obtained results are summarized as follows.

1. Phase diagram calculation using the ADAMIS database can be applied to optimize the blend ratio of Ag and Sn-17Bi-1Ag powders. It is suggested that the substantial chemical composition of Bi should be less than 4.3at.% to prevent the formation of the low-temperature eutectic of (Bi) and (Sn) at 139.5°C.



**Figure 6.** Result of DSC measurement of blended #2 samples after the TLPS process under the condition of  $T_{max} = 300^\circ\text{C}$  and  $t_h = 10\text{min}$ .



**Figure 7.** BSE images of microstructure of #2F, #2M and #2C samples after the TLPS process under the condition of  $T_{max} = 300^{\circ}\text{C}$  and  $t_h = 10\text{min}$ .

TLPS processed reactants are expected to endure a high-temperature environment up to  $250^{\circ}\text{C}$ .

2. The TLPS process at  $300^{\circ}\text{C}$  for 10min results in the formation of a  $10\ \mu\text{m}$   $\epsilon\text{-Ag}_3\text{Sn}$  IMC layer between Ag and a molten Sn-17Bi-1Ag alloy. Under this condition, the size of Ag powder particles should be less than  $20\ \mu\text{m}$  in diameter.

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