

# Influence of Supercooling on Formation of Primary Phase

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**Abstract.** It is reported actual volume fraction of primary phase in alloys is larger than the equilibrium value. Larger volume fraction of the primary phase may cause shrinkage cavities and surface or internal cracks. Although control of solidified structure is important for the quality of cast products, this problem has not been elucidated. Taking these results into account, this study has been carried out in order to comprehend a phenomenon of larger volume fraction of primary phase. Sn-Pb alloy has been used as a test alloy and to examine the relation between supercooling for nucleation and the volume fraction of primary phase has been mainly characterized. Actually, volume fraction of primary phase in Sn-Pb alloy is larger than that of lever rule. It was also observed that the volume fraction of  $\beta$ -Sn decreases with decreasing the supercooling in early stage of solidification. In the final stage of solidification, however, the effect of supercooling on volume fraction of primary phase is small. Furthermore, when the supercooling was low, volume fraction of primary phase was slowly increased.

## 1. Introduction

Recently, it has been reported that the actual volume fraction of primary  $\beta$ -Sn ( $f_{\beta\text{-Sn}}$ ) is larger than the equilibrium value in Sn-base alloys, which are the candidates for lead-free solders. For example, in Sn-1.27 mass% Ag alloy, the volume fraction of primary  $\beta$ -Sn was 0.784. In these cases,  $f_{\beta\text{-Sn}}$  calculated from equilibrium diagram is 0.65. Therefore, the actual  $f_{\beta\text{-Sn}}$  was 0.19 larger than prediction. The fact that  $f_{\beta\text{-Sn}}$  exceeds the equilibrium value is universal regardless of species of alloys and composition [1]. Larger  $f_{\beta\text{-Sn}}$  may cause shrinkage cavities and surface or internal cracks, since the volume of remaining liquid is too small to fill in the volume change due to solidification. Therefore, this problem may critically influence mechanical properties and significantly decrease reliability of solders.

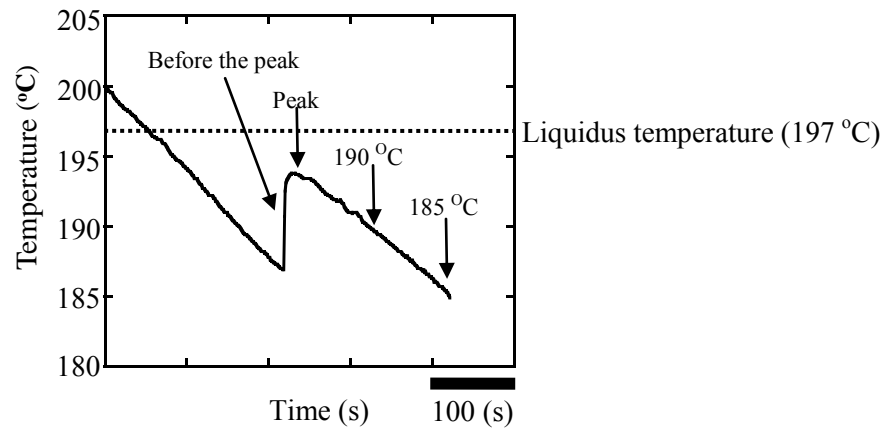
It is considered that  $f_{\beta\text{-Sn}}$  depend on the supercooling for nucleation ( $\Delta T$ ) [2]. Therefore, the objective of this study was to clarify the relationship between  $\Delta T$  and  $f_{\beta\text{-Sn}}$ . Time-dependent  $f_{\beta\text{-Sn}}$  has been characterized, changing  $\Delta T$ .

## 2. Experimental procedure

5g of Sn-25mass% Pb alloy was melted in an alumina crucible and kept at 300 °C for 30 minutes. Then, the temperature of the furnace was lowered at a constant cooling rate of 3 °C/min. The temperature of the specimen was directly measured by a K-type thermocouple installed in the crucible. When the temperature was below the liquidus temperature (=197 °C), a stainless steel rod was inserted as a trigger for nucleation at predetermined supercooling ( $\Delta T$ ). The  $\Delta T$  used in this study ranged 0.1 °C



to 20 °C. After nucleation, the specimen was fallen into a water bucket at predetermined timing to quench the structure. A typical thermal history is shown in figure 1 and timing of quenching is also indicated: before the peak, peak, 190 °C and 185 °C. Since the cooling rate of quenching was 200 °C /sec, it was possible to realize the solidified structure before the quenching. The specimen was vertically cut at the center and polished. After being etched by a dilute aqua regia, solidified structure was observed by a FE-SEM and  $f_{\beta\text{-Sn}}$  before quenching was measured by an image processor.

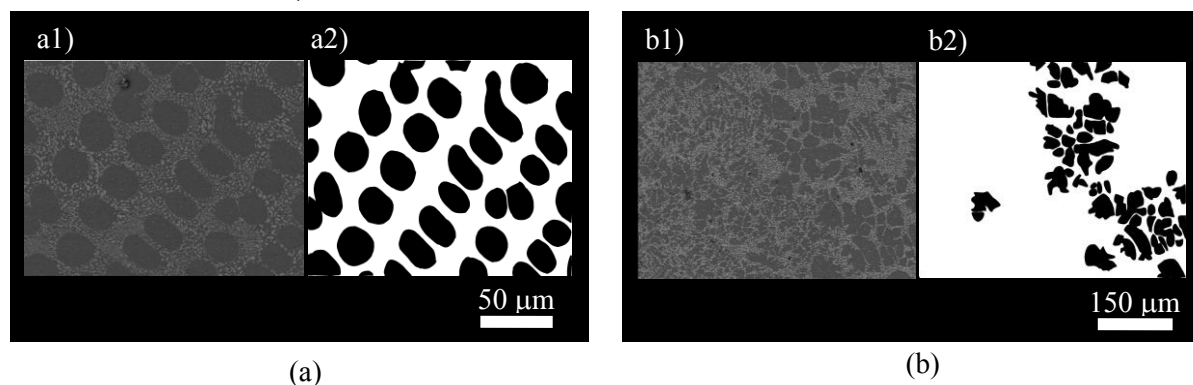


**Figure 1.** A typical thermal history and Timing of quenching.

### 3. Experimental results

Two examples of SEM images are shown in figures 2(a) and (b). In case of  $\Delta T=20$  °C and quenched at 185 °C, solidified structure is shown in figure 2(a). In case of  $\Delta T=1$  °C and quenched at before the peak, solidified structure is shown in figure 2(b). The primary phase was distinguished from size and morphology to measure the volume fraction of primary ( $\beta\text{-Sn}$ ) that had solidified before quenching, they were realized and marked by hand (figure 2. a2, b2). After this,  $f_{\beta\text{-Sn}}$  was measured using an image processing software. For example,  $f_{\beta\text{-Sn}}$  in figure 2 a2) and in figure 2 b2) are 0.47 and 0.17, respectively.

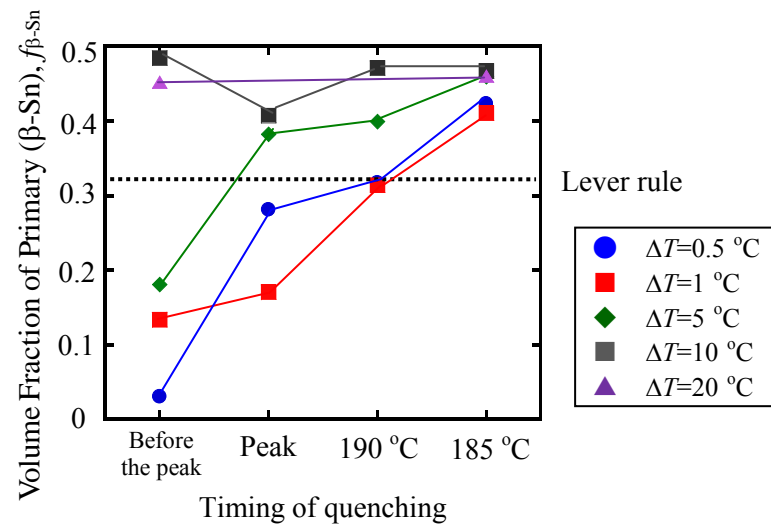
The relationship between quenching timing and  $f_{\beta\text{-Sn}}$  is shown in figure 3. In early stage of solidification, it was observed that the  $f_{\beta\text{-Sn}}$  increased with increasing the supercooling. In case of small  $\Delta T$ ,  $f_{\beta\text{-Sn}}$  increased gradually with time. On the other hand, in case of large  $\Delta T$ ,  $f_{\beta\text{-Sn}}$  was large just after the nucleation. Finally,  $f_{\beta\text{-Sn}}$  was larger than equilibrium value regardless of  $\Delta T$ .



**Figure 2.** SEM images of solidified structure.

(a) quenched at 185 °C ( $\Delta T=20$  °C),

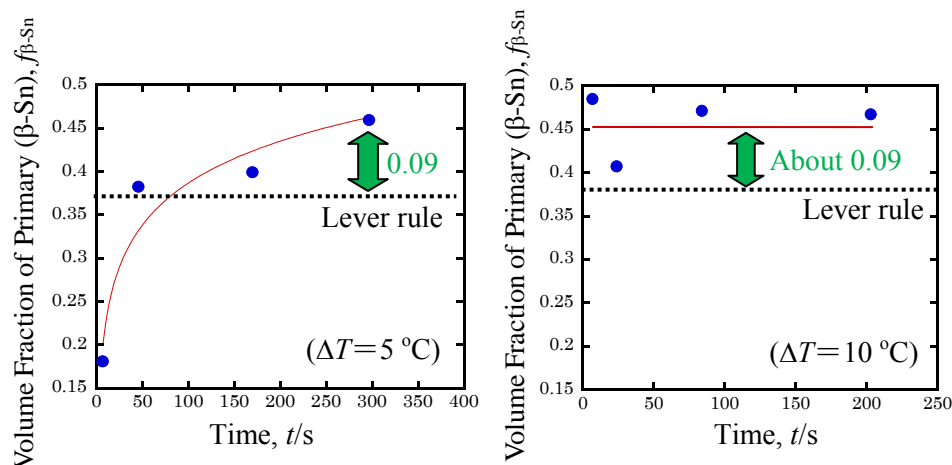
(b) quenched just after nucleation ( $\Delta T=1$  °C)



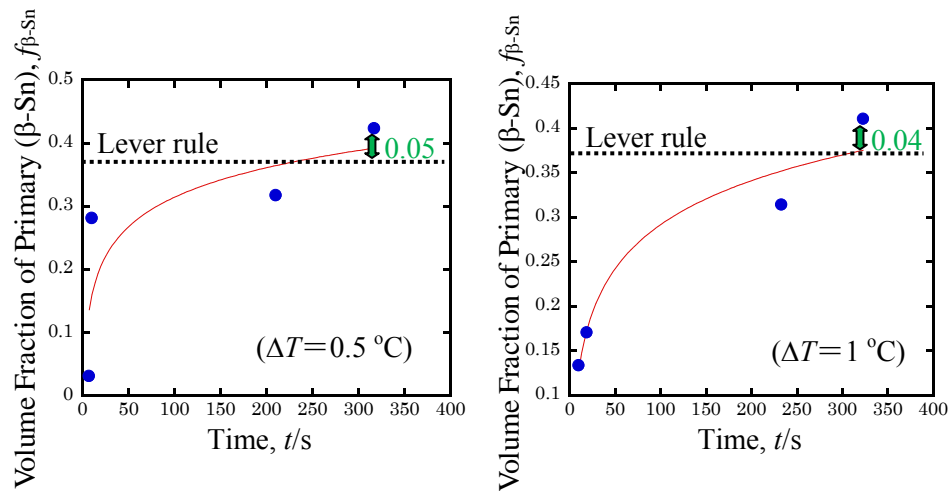
**Figure 3.** The relationship between  $f_{\beta-Sn}$  and timing of quenching.

Now, the time ( $t$ ) is defined as the time elapsed from the nucleation for primary  $\beta$ -Sn. The relationship between  $t$  and  $f_{\beta-Sn}$  in case of large  $\Delta T$  is shown in figures 4, ( $\Delta T=5\text{ }^{\circ}\text{C}$ ) and ( $\Delta T=10\text{ }^{\circ}\text{C}$ ). The relationship between  $t$  and  $f_{\beta-Sn}$  in case of small  $\Delta T$  is shown in figures 5, ( $\Delta T=0.5\text{ }^{\circ}\text{C}$ ) and ( $\Delta T=1\text{ }^{\circ}\text{C}$ ). In case of  $\Delta T=10\text{ }^{\circ}\text{C}$ , the  $f_{\beta-Sn}$  exceeded equilibrium value within a few seconds. In case of  $\Delta T=5\text{ }^{\circ}\text{C}$ , the  $f_{\beta-Sn}$  exceeded equilibrium value 46 seconds after the nucleation. These results indicate that the  $f_{\beta-Sn}$  exceed equilibrium value in a short time if the molten metal was largely supercooled. Furthermore, the final  $f_{\beta-Sn}$  was 0.09 larger than the lever rule in both cases.

Comparing to the supercooling of 20 or 10  $^{\circ}\text{C}$ ,  $f_{\beta-Sn}$  gradually increased in case of 0.5 and 1  $^{\circ}\text{C}$ . At the final stage of solidification,  $f_{\beta-Sn}$  exceeded the equilibrium value, but it was 0.05 larger than the equilibrium value at most.



**Figure 4.** Relationship between  $t$  and  $f_{\beta-Sn}$  in case of large  $\Delta T$  (5  $^{\circ}\text{C}$ , 10  $^{\circ}\text{C}$ ).



**Figure 5.** Relationship between  $t$  and  $f_{\beta-Sn}$  in case of small  $\Delta T$  (0.5  $^{\circ}\text{C}$ , 1  $^{\circ}\text{C}$ ).

#### 4. Discussions

The present experimental study using a trigger can separate the nucleation and growth of primary  $\beta\text{-Sn}$ . As mentioned earlier, the important results are following two points.

- (1)  $f_{\beta-Sn}$  increased rapidly, when the  $\Delta T$  was large. But,  $f_{\beta-Sn}$  gradually increased when the  $\Delta T$  was low.
- (2) Final  $f_{\beta-Sn}$  was larger than equilibrium value regardless of  $\Delta T$ . But, strictly speaking,  $f_{\beta-Sn}$  was larger with increasing  $\Delta T$ .

The factors which affect  $f_{\beta-Sn}$  may be nucleation and growth. According to the classical nucleation theory, it is known that the frequency of nucleation for pure substance increases as  $\Delta T$  increases [3]. The amount of  $\Delta T$  discussed in the classical nucleation theory may be over 50  $^{\circ}\text{C}$  [4]. In present study, the range of  $\Delta T$  is 0.5 ~ 20  $^{\circ}\text{C}$ , which is too small for homogeneous nucleation. Actually in this experiment, a stainless steel rod was used for a trigger. The temperature of rod was room temperature and it promoted heterogeneous nucleation on the surface of the rod. Frequency of nucleation was not measured in this experiment, though, it may not depend on the  $\Delta T$  in the range of this study.

There have been some experimental studies to relate the  $\Delta T$  and the growth velocity in pure substance. According to these results, it is known that the growth velocity is approximately proportional to  $\Delta T^2$  [5]. Therefore, it is reasonable that  $f_{\beta-Sn}$  slowly increased when the  $\Delta T$  was small because dendrite grew slowly. In a similar way, it is valid  $f_{\beta-Sn}$  is high in the initial stage of solidification in case of large  $\Delta T$ . The reason that the final  $f_{\beta-Sn}$  increased with increasing  $\Delta T$  has been uncertain. Further, the reason that the  $f_{\beta-Sn}$  is larger than the equilibrium value has been uncertain.

#### 5. Conclusions

To comprehend the reasons that  $f_{\beta-Sn}$  is larger than equilibrium value, the present experimental study was carried out focusing on relationship between  $f_{\beta-Sn}$  and  $\Delta T$ . From this study, following results were clarified.

- (1) In Sn base alloys, final  $f_{\beta-Sn}$  was larger than equilibrium value regardless of  $\Delta T$ .
- (2)  $f_{\beta-Sn}$  in case of large  $\Delta T$  tend to be larger than that in case of small  $\Delta T$ .
- (3) Dendrite growth velocity may influence  $f_{\beta-Sn}$  rather than frequency of nucleation.

**References**

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