ABNORMAL SOLIDIFICATION OF Pb-Sn ALLOY INDUCED BY LIQUID STRUCTURE TRANSITION

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The purpose of this paper is to investigate the effect of liquid-liquid structure transition on the solidification behaviour and solidification structure for Pb-Sn alloys. Furthermore, we attempt to control the solidification on the base of the liquid structure transition. From our prior investigation results, it is shown that a temperature-induced discontinuous liquid-liquid (L-L) structure transition could occur in some binary alloys, at a temperature range much above the liquidus. This transition is irreversible during cooling procedure. In the present paper, it has been proved that the solidification behaviour and solidified microstructure of Pb-Sn alloy depend on whether the melt is prepared above the critical temperature or under that. It is found that the solidification undercooling degree of the alloy prepared above the critical temperature is several times larger than that prepared under this temperature. High undercooling leads to a finer solidification microstructure.

K e y w o r d s: Pb-Sn alloy, L-L structure transition, solidification behaviour, solidified microstructure

1. Introduction

In recent years, lots of achievements have been made in the solidification theory and technology. It has been found that the solidification structure will become finer when the melt is held at a high temperature. However, most of these experiments are designed to hold a melt at several temperatures above melting point and then solidify. By comparing the solidified structures, the authors can conclude that the structure will be finer after it is held above a certain temperature. These results have a deep significance in engineering practice. To explore the intrinsical reason of the phenomena, the paper investigates the effect of liquid structure transition

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on the solidifying behaviour and solidification structure. This will be useful for the further investigation of solidification of other alloy systems.

In our earlier work [1–3], by means of a revised internal friction technique, a temperature-induced discontinuous L-L structure transition has been found to occur in some molten alloys, e.g. Pb-Sn, Pb-Bi and In-Sn, much above liquidus. This transition is irreversible and the new structure after the transition would remain in the melts during the whole cooling process. This intriguing phenomenon was verified by DSC [1] and XRD [4] experiments. Since solidification means the rearrangement of atoms into a steady structure, assume that the above found L-L transition must have some effects on the solidification behaviour and solidified structure. Based on this assumption, the effects of the L-L transition on the solidification behaviour and solidified structures were investigated for Pb-Sn alloys. And surprisingly, some abnormal phenomena about solidification behaviour and solidified microstructure of Pb-Sn alloys are observed.

2. Experiments

Corresponding to the discontinuous L-L structure transition, the internal friction-temperature (IF-T) peak occurs in the IF-T curves. For each Pb-Sn alloy, the peak temperature ranges and peak positions are listed in Table 1. In this paper, Pb-61.9%Sn and Pb-80%Sn alloy are selected for experiments to stand for eutectic and non-eutectic compositions. Melting and holding temperatures for Pb-Sn alloys are chosen according to the internal friction transition temperatures, that is, 550 ℃ (below the L-L structure transition temperature) and 800 ℃ (above the L-L structure transition temperature) before casting. Figure 1 shows the Pb-Sn phase diagram and the composition for present experiments, in which it is very clear that the eutectic temperature is 183 ℃, and the liquid-solid transition temperature of Pb-80%Sn is 203 ℃.

Table 1. Internal friction-temperature curve parameters and holding temperatures of Pb-Sn alloy

Alloy	Temperatures range of IF-T peak/℃	Peak position/℃
Pb-61.9%Sn	575–800	670
Pb-80%Sn	610–720	650
Pb-20%Sn	575–700	620
Pb-40%Sn	600–850	740

Weighing 30 g, each Pb-Sn alloy sample was prepared from pure (99.9 wt.%) lead and tin. After melting, the melts were held at 550 ℃ or 800 ℃ for 5 hours.

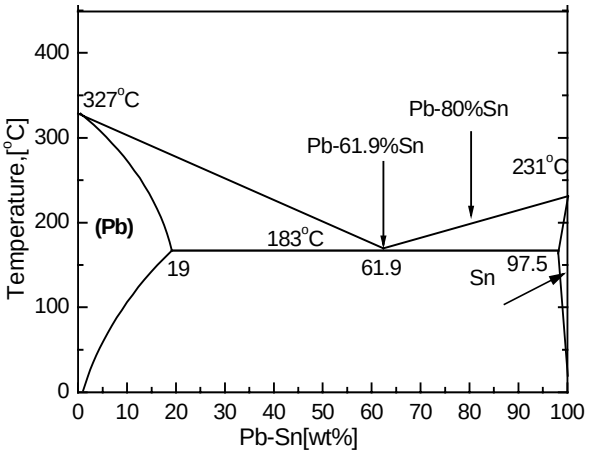

Fig. 1. The Pb-Sn phase diagram.

During the entire melting process, the sample was covered with B_2O_3, which is well known as a purifying agent besides as a cover. Afterwards, the melt was directly cast into an iron mould with the exterior dimensions of ø 50 × 40 mm and the interior dimensions of ø 17 × 25 mm. And simultaneously, by a NiCr-NiSi thermocouple, the temperature-time (T-t) curve was recorded. Then the solidified samples were used to observe the microstructures.

In the present paper, for convenience, A1 and B1 represent the melts prepared at the temperature of 550 ℃ – 5 h for Pb-61.9%Sn and Pb-80%Sn, respectively; and A2 and B2 represent the melts prepared at the condition 800 ℃ – 5 h for Pb-61.9%Sn and Pb-80%Sn, respectively.

3. Results and discussion

T-t curves of solidification process of the Pb-Sn specimens are shown in Fig. 2 (for Pb-61.9%Sn) and Fig. 3 (for Pb-80%Sn), and the related solidification parameters are listed in Table 2 (for Pb-61.9%Sn) and Table 3 (for Pb-80%Sn), in which T^{S} denotes the beginning temperature of solidification, T^{EN} the ending temperature of solidification and ΔT^{N} denotes the undercooling degree of nucleation.

From Tables 2 and 3 and Figs. 2 and 3, it is shown that the characteristics of solidification of the samples at different melting conditions are dissimilar. Apparently, there are some diverse phenomena in the solidification process, which can be described in detail as follows:

For Pb-61.9%Sn, it can be concluded from Table 2 easily that ΔT^{N} of A1 is 3 ℃ and ΔT^{N} of A2 is 15 ℃; also obviously, the undercooling degree for nucleating

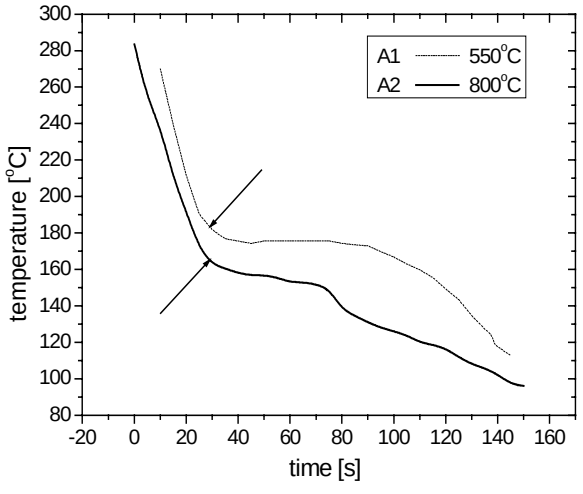

Fig. 2. Temperature-time curves of Pb-Sn61.9% after melting at 550 °C (5 h) and 800 °C (5 h). (The arrows in the figure indicate the beginning of the solidification.)

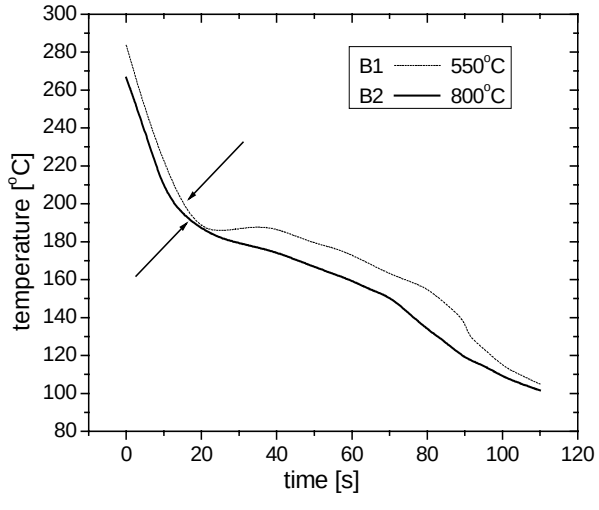

Fig. 3. Temperature-time curves of Pb-Sn80% after melting at 550 °C (5 h) and 800 °C (5 h). (The arrows in the figure indicate the beginning of the solidification.)

and growing of A2 is in the range of 3–19 °C but that of A1 is in the range of 18–34 °C. Moreover, the solidifying time of A1 (about 8 seconds) is much longer

Table 2. Effect of different holding temperatures on the solidification transition of Pb-61.9%Sn

Holding temperature/℃	T^{S}/℃	T^{EN}/℃	ΔT^{N}/℃	The main undercooling range for nucleating and growing/℃
550 (Before IF-T peak)	180	173	3	3–19
800 (After IF-T peak)	165	150	18	18–34

Table 3. Effect of different holding temperatures on the solidification transition of Pb-80%Sn

Holding temperature/℃	T^{S}/℃	T^{EN}/℃	ΔT^{N}/℃	The main undercooling range for nucleating and growing/℃
550 (Before IF-T peak)	199	147	4	4–43
800 (After IF-T peak)	190	137	13	13–61

than A2 (about 5 seconds). So, it could be deduced from the solidification time that the nuclei number of A1 is certainly lower than that of A2, because more grains would attach to each other in shorter time, which restrains them from growing any more. Besides, the curve of A1 has risen by 2℃ in eutectic transition while that of A2 descends continuously and slowly, which indicates that the latter one releases less heat.

As to Pb-80%Sn, according to the phase diagram and the lever rule, the melt firstly separates out β-Sn solid solution and then the remainder melt (less than half of the sample) transits into eutectic (α-Pb + β-Sn). As a result, the released quantity of heat in certain moment is smaller in solidification and there is no platform to be observed in the curves of B1 and B2. From Table 3, it is clear that ΔT^{N} of B2 (13℃) is greater than B1 (4℃), similar to Pb-61.9Sn% melt. The undercooling range for nucleating and growing of B2 is 13–61℃ but that of B1 is 4–43℃. Furthermore, comparing the curves of Pb-80%Sn alloy, one can find that the solidification time of B2 is shorter than that of B1. It is the same as in the case of Pb-61.9%Sn melt.

From the comparisons above, it is confirmed that the effects of liquid microstructure change on the solidification behaviour of Pb-Sn alloy are evident, for the undercooling degree and the nuclei number in solidification are different evidently between the specimens that were prepared above and below the temperature of IF-T peak. Some further studies on Pb-61.9%Sn and Pb-80%Sn are performed to reveal the effect of L-L structure transformation on the solidified microstructure.

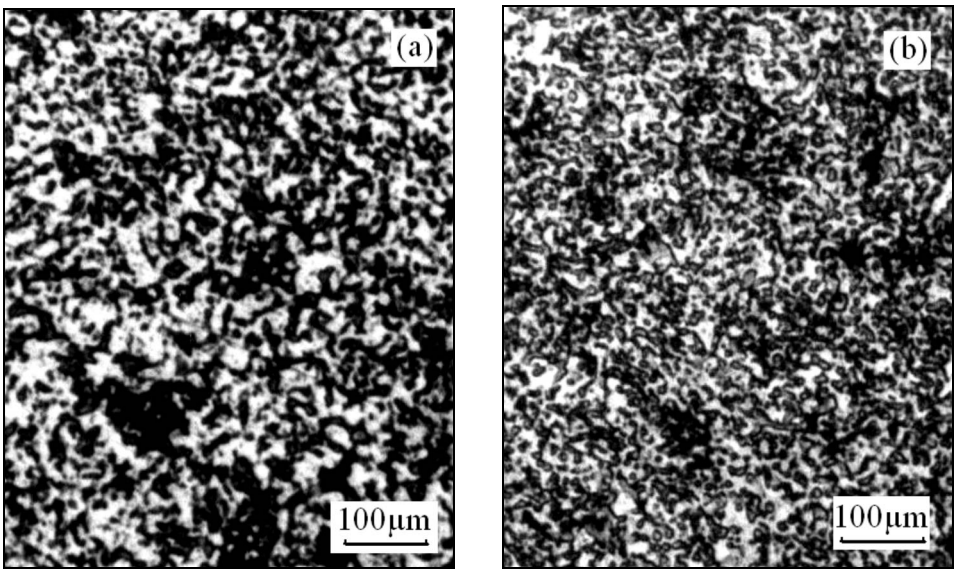

Fig. 4. The as-cast microstructure of Pb-61.9%Sn alloy: (a) holding at 550 ℃, (b) holding at 800 ℃.

Figures 4 and 5 show the solidified microstructures of Pb-61.9%Sn and Pb-80%Sn after holding 5 hours at 800 ℃ or 550 ℃. From these figures, it is clear that the solidified microstructure of A2 or B2 is much finer than that of A1 or B1. Furthermore, the solidified structures are all irregularly discrete when the melts are cooled rapidly in the metallic mould, which is different from the common intergrowth of metal-metal alloy.

In equilibrium structure, Pb-Sn alloy consists of intergrowth structure of Pb solid solution and Sn solid solution. The positive excess enthalpy of Pb-Sn [5] indicates repulsive interactions between Pb and Sn. Furthermore, the existence of local crystal orderings in melts has been proposed based on results of experiments [6–9] and theoretical analysis from the standpoint of thermodynamics [7]. It is considered that the short-range orders corresponding to the crystal structures remain still in the melts a little above the melting point. So it can be concluded that the liquid Pb-Sn alloy consists mainly of Pb-Pb clusters and Sn-Sn clusters little above the melting point. With the increasing temperature, atoms obtain more and more kinetic energy and Pb clusters and Sn clusters split into smaller ones gradually. Up to the critical temperature, the energy of these atoms is large enough to overcome the energy barrier so that the Pb-Pb and Sn-Sn atomic bonds in original phases are broken continuously. At the same time, the new Pb-Sn atomic bonds come

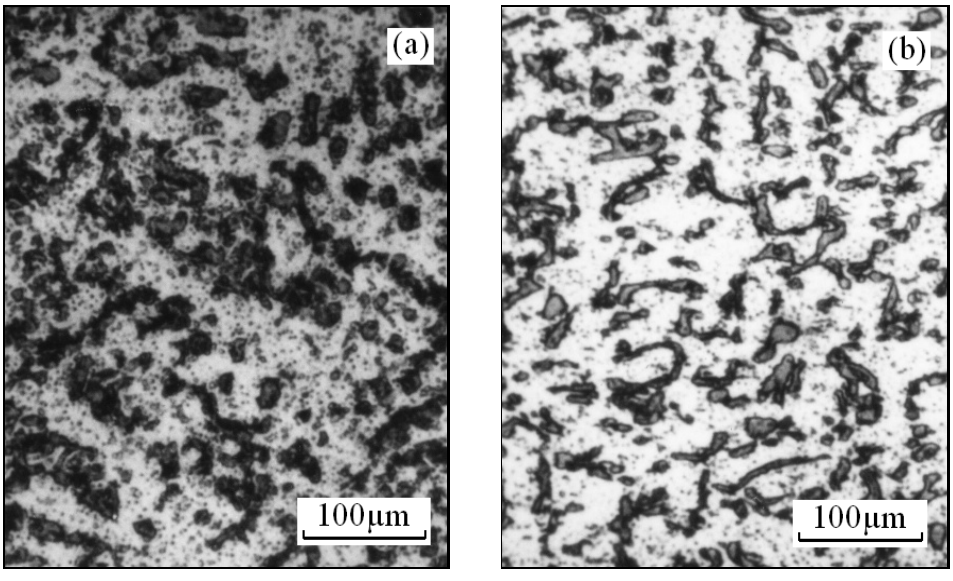

Fig. 5. The as-cast microstructure of Pb-80%Sn alloy: (a) holding at 550 ℃, (b) holding at 800 ℃.

into being, by which the relatively homogeneous liquid phase nucleates and grows. So the liquid-liquid structure transition takes place, that is L′ (rich in Pb) + L″ (rich in Sn) → L (Pb-Sn). Thus the liquid melt consists of smaller Pb-Sn clusters and also becomes more disordered above the critical temperature. This transition is irreversible and the new structure (L) after the transition would remain in the melts during the whole cooling process.

Therefore, under the L-L structure transition temperature, there are Pb-Pb and Sn-Sn clusters in the melt, which is short-range ordered structure. This liquid structure (L′ + L″) is beneficial to nucleating and growing during the solidification procedure because of the convenient fluctuation component, and thus the nucleation undercooling degree is small. Whereas above the IF-T peak temperature, the Pb-Pb and Sn-Sn clusters transform into Pb-Sn clusters, which leads to smaller and more disordered clusters and then makes it difficult to nucleate. So, greater undercooling degree is needed for nucleating on this condition. Furthermore, according to the classical nucleation theory, the greater undercooling degree, the greater nucleating rate is, and the finer solidified structure will be.

4. Conclusions

The solidification behaviour and solidified microstructure of the Pb-Sn melts prepared below and above the L-L structure discontinuous transition temperature

have been investigated in this paper. The results show that the solidification undercooling degree of Pb-61.9%Sn and Pb-80%Sn both increases by several times and the nuclei number becomes higher on the condition that Pb-Sn alloys are melt above the critical temperature, which causes finer solidified structure evidently. It implies that the temperature-induced L-L structure transition has great effects on solidification behaviour and solidified structures. So, it is obviously effective to control solidification based on the results of liquid structure transition. Furthermore, this finding is beneficial to the further understanding of the micro-mechanism of solidification, and also helps to improve the solidified morphology and the mechanical properties in practical engineering.

Acknowledgements

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