Liquid-liquid structure transition and its effect on solidification of Sn-Sb alloy

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Abstract

The temperature dependence of electrical resistivity of liquid Sn-Sb alloys has been investigated in several heating and cooling cycles, using D.C. four-probe method. Obvious reversible changes are observed on resistivity-temperature curves of the investigated Sn-Sb alloys, and there are clear turning points both on heating and cooling process in several experimental cycles. However, the temperature of turning points and the resistivity change trend in the first cycle heating are different from those of the subsequent cooling and heating cycles; it is suggested that there are temperature-induced liquid-liquid transitions in Sn-Sb alloys, moreover the transitions are partly reversible. The effect of the liquid-liquid structure transition (L-LST) on the solidification behaviour and morphology of Sn-Sb80wt.% is further studied. The results show that solidification behaviour and solidified microstructure would be distinct when the melt experienced the L-LST.

Key words: Sn-Sb alloys, electrical resistivity, reversible liquid-liquid transition, solidification behaviour

1. Introduction

Liquid-liquid structural change has become a common concern in liquid physics these years, which enriches the phenomenology in liquid physics and sheds light on the structure and property of liquid materials. In the last decade, temperature or pressure dependence of liquid-liquid structure transitions (L-LST) was put forward in some alloys by different experimental methods and theoretical calculations [1–10]. Moreover, the reversible L-LST in the molecular liquid triphenyl phosphite [11] has been reported recently, which makes the existence of L-LST more convincing.

Sb-based alloys are subject of numerous investigations, since the mean free path of Sb is slightly greater than its interatomic distance, which is the limit range of Ziman theory in the nearly free electron model. The abnormal behaviour of resistivity in pure antimony and Bi-Sb alloys has been reported [12, 13], respectively, which indicates that liquid-liquid structure transitions probably take place in liquid Sb and Bi-Sb melts. However, whether this phenomenon is reversible is still unknown. Although considerable attention has been given to the research on Sn-Sb alloys [14–17], papers on Sn-Sb alloys seldom concentrate on L-LST and its reversibility.

It is well known that the melt structure has a direct and significant effect on the solidification microstructure and properties of metallic materials [18–22]. In recent years, overheating, melt thermal treatment, melt thermal-rate treatment have become the most active areas in condensed matter physics and material processing, and some achievements have been acquired. Usually, different solidification structure is owed to the difference of the melt structure, and the essence of the effect needs to be further studied.

In this paper, the electrical resistivity of liquid Sn-Sb alloys has been measured continuously in several heating and cooling cycles in order to probe the reversibility of L-LST. The results showed that there were nonlinear changes on the resistivity-temperature (ρ-T) curve at the temperature of several hundred degrees above corresponding liquids both in heating and cooling cycles. In the isothermal experiment, abnormal change in the curve of resistivity versus time

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(ρ-t) occurs after holding at 750 ℃ for 75 min. Since resistivity is one of the physical properties sensitive to structure, the unusual change of resistivity indicates that liquid-liquid transitions probably take place in Sn-Sb melts. Based on the resistivity experiment results, the effect of the L-LST on solidification of Sn-Sb80wt.% alloy is also studied further.

2. Experimental details

Sn-Sb42wt.%, Sn-Sb50wt.%, Sn-Sb65wt.%, and Sn-Sb80wt.% were chosen for the investigation. Each sample was prepared from pure tin and antimony (99.99 wt.%) granules in a ceramic crucible using an electrical resistance furnace. After melting and hold at the temperature of 650 ℃ covered with B_2O_3 for 30 minutes, the melts were poured into quartz cells for the resistivity experiments which were carried out in purified argon media (5N). The heating and cooling rate was set as 5 ℃ min^{-1}. According to the temperature range of the anomalous changes on ρ-T curve, isothermal experiment has been carried out on Sn-Sb80wt.% melt held at 750 ℃ for 5 hours, the resistivity-time curve was recorded. The resistivity measuring details are the same as described elsewhere [23, 24].

Based on the result of isothermal experiments, 750 ℃ was chosen as melting and holding temperature. Two samples (A and B) with identical composition and weight (20.000 g) were prepared for the alloy (Sn-Sb80wt.%), then sample A and sample B were melted and held at 750 ℃ for 1 hour and 3 hours, respectively, in a ceramic crucible. In order to prevent samples from volatilization and oxidation, the samples were covered with B_2O_3 during the entire melting process. Afterwards, the melts were poured into a metal mould for solidification.

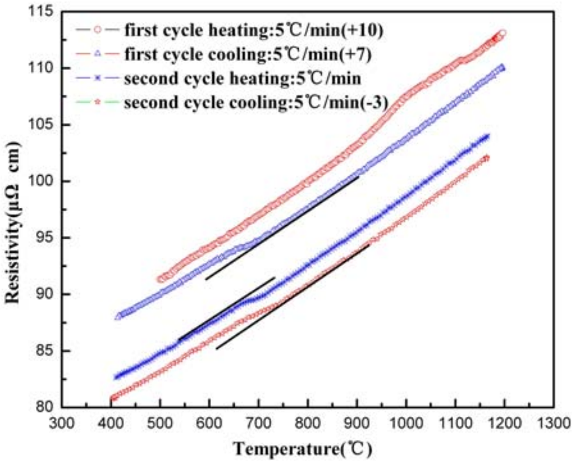

Fig. 1. The resistivity-temperature curves of Sn-Sb42wt.% alloy in two heating and cooling cycles.

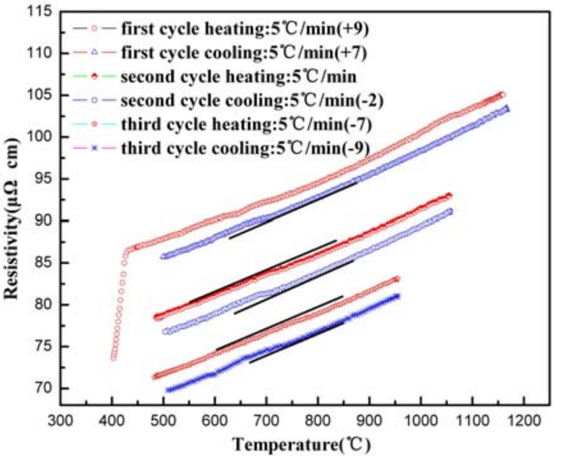

Fig. 2. The resistivity-temperature curves of Sn-Sb50wt.% alloy in three heating and cooling cycles.

3. Results and discussion

Figures 1–4 show the ρ-T curves of Sn-Sb melts. As seen in the figures, the resistivity of all the melts changes obviously within certain temperature range both on heating and cooling process. Comparing the character of first cycle heating ρ-T curve with that of subsequent cooling and heating ones, we can find that the turning points and the change trend on ρ-T curve are different, and evident reversible changes can be observed on ρ-T curves after the first cycle heating. Since resistivity is one of the physical properties sensitive to structures, it is presumed that two sorts of L-LST exist in Sn-Sb melts, namely, irreversible L-LST in the first cycle heating and reversible L-LST in the subsequent heating and cooling cycles.

Generally, it may be accepted that the atomic bonds in crystals are only partly broken on melting and the short-range orders similar to the corresponding solid crystal still remain in liquids [25–27]. As is well known, Sb is a semi-metal. It has been reported that a semi-metal to metal change occurs on Sb melting, with its coordination number increase from 3 in crystalline state to 4.6 to 8.7 in liquid state, however, this value remains well below the general simple liquid metal (about 11). It has been proved experimentally and theoretically that there is a clear shoulder on the high-Q side of the first peak of $S(Q)$ at 660 ℃ [28], and this shoulder disappears at 800 ℃ in liquid Sb. These results suggest that some metastable $(Sb)_n$ short-range orders (SROs) with covalent characteristic may remain in liquid Sb at lower temperature. With temperature increasing, the metastable SROs will gradually change into stable SROs. For

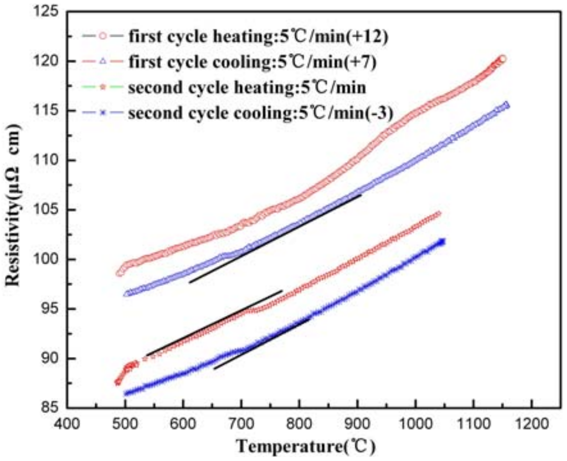

Fig. 3. The resistivity-temperature curves of Sn-Sb65wt.% alloy in two heating and cooling cycles.

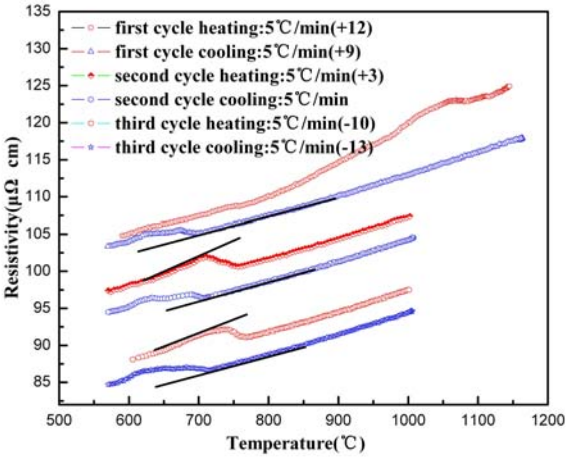

Fig. 4. The resistivity-temperature curves of Sn-Sb80wt.% alloy in three heating and cooling cycles. *Note:* The positive or negative values in the brackets after each cycle mean that the practical ordinate value of the ρ-T curve is plus or minus a certain value in order to avoid the curves overlapping.

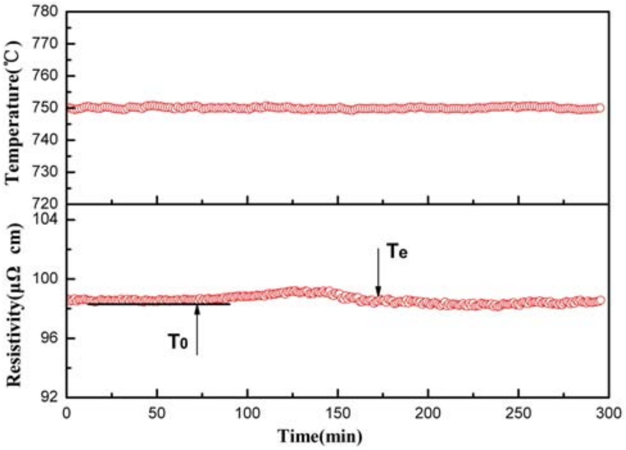

Fig. 5. The resistivity-time curves of Sn-Sb80wt.% at 750 ℃.

Sn-Sb alloys, it is reasonable to assume that there are probably many similar metastable SROs (such as Sn-Sn, Sb-Sn SROs, $(\mathrm{Sb})_{\mathrm{n}}$ SROs) in the melts at a low temperature above the liquidus. With the temperature further rising, these metastable SROs are broken until the melt reaches a stable state, at the same time, new liquid structure builds up. This metastable to stable transition in liquid Sn-Sb alloys is irreversible, which results in the different character of ρ-T curve between first cycle heating and that of the subsequent cycles.

From what has been discussed above, we can assume that liquid Sn-Sb alloys reach a stable state and build a new structure after the first cycle heating. The stable liquid Sn-Sb alloys include some SROs with reversible change character, i.e. they can reassemble at the L-LST temperature on cooling and break at the L-LST temperature on heating to present the reversible characteristic on ρ-T curves. According to [29, 30], the neutron scattering experiments have been done to investigate the structure of liquid Sn. The experimental results show that there is a clear shoulder on the high-Q side of the first peak of $S(Q)$ at 300 and 500 ℃, and even at 1600 ℃, such a shoulder may still be present. As we know, the shoulder is the sign of covalent bond. These features for liquid Sn indicate that some tetrahedral SROs with covalent characteristic may remain in liquid Sn at lower temperature, and at least the fragments of tetrahedral unit may persist even at high temperatures in liquid Sn [30, 22]. Based on the result of neutron scattering experiment [28], we can presume that the tetrahedral SROs with covalent characteristic in liquid Sn and Sn-Sb melts may be the main cause of the reversibility of L-LST.

For the isothermal experiment of Sn-Sb80wt.%, the curve of resistivity versus time (ρ-t) is recorded in Fig. 5. As seen in Fig. 5, an abnormal change in the ρ-t curve occurs after holding at 750 ℃ for 75 min, which indicates that structure change also takes place in the melt during the isothermal process. Through the tangent method, we set t_0 (75 min) and t_{e} (175 min) as the transition beginning and ending time, respectively. In order to explore the effect of irreversible L-LST on solidification, and based on the result of Sn-Sb80wt.% isothermal experiment, corresponding solidification experiments have been carried out, the results are shown in Fig. 6. Figure 6 gives the photomicrographs of Sn-Sb80wt.% solidified from different melt states [before (sample A – 750 ℃ for 1 hour) and after (sample B – 750 ℃ for 3 hours) L-LST]. Moreover, the results of corresponding X-ray diffraction patterns are shown in Fig. 7. According to Sn-Sb equilibrium phase diagram [31], Sn-Sb80wt.% is far from the peri-

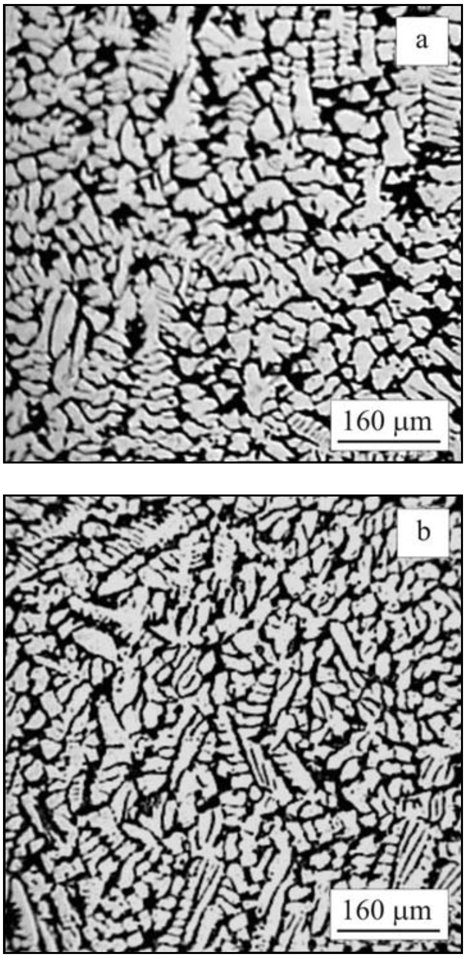

Fig. 6. Solidification structures of Sn-Sb80wt.% held at 750 °C (cast into steel mould): (a) sample A, (b) sample B.

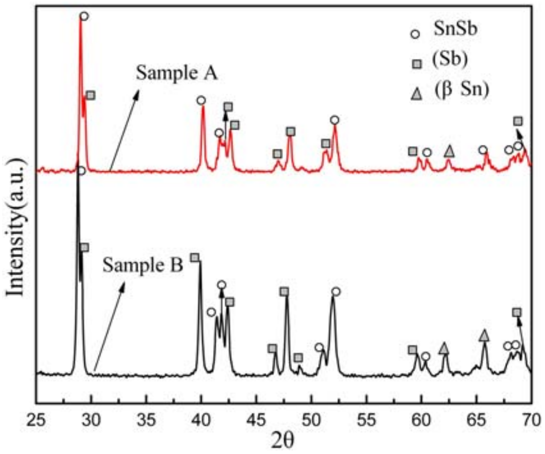

Fig. 7. X-ray diffraction of Sn-Sb80wt.% held at 750 °C (cast into steel mould).

tectic point composition, the primary phase begins to precipitate when the melt is cooled below 568.80 °C (liquidus), and the peritectic reaction will occur when the temperature is down to 425 °C, and the primary (Sb) and peritectic phase (SnSb) will coexist at room temperature. But as a matter of fact it is far from the equilibrium state, as seen in Fig. 7, the (βSn) phase is also present. In Fig. 6, the white grey area is primary phase (Sb) and peritectic phase (SnSb), and the dark area is (βSn) phase. Comparing Fig. 6a with Fig. 6b, we can find that the microstructure becomes finer after solidifying from the melt experienced the L-LST (sample B). Selecting several 1 mm^2 areas of view, we calculate the average number of grains in the area unit. For sample A the grain number is 161, while the grain number of sample B is 205, the solidification structure of sample B is finer evidently. Based on the XRD experiment results, by calculating, the amount of peritectic phase in sample B is less than that of sample A. It should be pointed out that both sample A and sample B cooled down from 750 °C at the same cooling rate. So the effect of the casting temperature and cooling rate difference can be ignored.

From what has been discussed above, we know that the character of L-LST in the isothermal experiment is similar to that of the first cycle heating, that is to say, the structure change in the insulation process is also irreversible. The irreversible L-LST must have some effect on solidification behaviour and microstructure. When the melt is held at 750 °C for 3 hours, the metastable SROs similar to the corresponding solid may have been broken up and the melt becomes more uniform, disordered and stable. These transitions destroy the advantageous conditions for nucleation and produce a lot of free atoms. According to the relation between critical radius and undercooling in classical nucleation theory, for sample B, the smaller and disorder clusters cannot grow to the critical nucleation size conveniently unless at a greater undercooling. It was suggested that greater undercooling resulted in the obvious increment of nucleation rate during solidification process for sample B (after L-LST) and the grain size was refined evidently.

4. Conclusions

In summary, the electrical resistivity of Sn-Sb melts with different compositions has been measured, the anomalous change on the ρ-T curve indicates that there are two sorts of liquid-liquid structural transition in liquid Sn-Sb alloys – irreversible in the first cycle heating and reversible in the subsequent cycles.

Solidification experiment results show that the size of primary phase decreases and the microstructure becomes finer when solidifying from the melt which experienced the L-LST. It proves that the L-LST has great effect on solidification behaviour and solidified microstructures.

Acknowledgements

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