Int J Thermophys (2009) 30:1040–1047
DOI 10.1007/s10765-009-0612-4

Temperature-Induced Reversible Change of Electrical Resistivity in Sn–Bi Melts

Xian-Fen Li · Cheng-Ming Hu · Fang-Qiu Zu ·
Zhong-Yue Huang · Ming-Quan Liu

Abstract Using a dc four-probe method, the temperature dependence of the electrical resistivity of liquid Sn–Bi alloys has been investigated. The results show that there are clear turning points both on heating and cooling for several experimental cycles. Since the electrical resistivity is one of the physical properties sensitive to structure, the unusual change of the resistivity indicates that liquid–liquid transitions (LLT) probably take place in Sn–Bi melts. Moreover, the transitions are reversible. Compared with the experimental results for pure Sn and Bi, it is assumed that Sn plays an important role in the reversible liquid–liquid transitions.

Keywords Electrical resistivity · Reversible liquid–liquid transition · Sn–Bi alloy

1 Introduction

An understanding of the structure and property of liquids is closely related to the progress of science and technology in many fields, such as condensed matter physics, material sciences, life sciences, metallurgy, etc. In the past 10 years, the temperature or pressure dependence of liquid–liquid transitions (LLT) was observed in some alloys by different experimental methods and theoretical calculations [1–9]. Moreover, a reversible LLT in the molecular liquid triphenyl phosphite [10] has been reported recently, which makes the existence of LLT more convincing.

Although considerable attention has been devoted to research on the LLT, papers on the LLT seldom concentrate on the reversibility of LLT, especially in liquid alloys. As we know, the electrical resistivity is one of the physical properties sensitive to

---

X.-F. Li · C.-M. Hu · F.-Q. Zu (✉) · Z.-Y. Huang · M.-Q. Liu
Liquid/Solid Metal Processing Institute, School of Materials Science and Engineering,
Hefei University of Technology, Hefei 230009, People's Republic of China
e-mail: fangqiuzu@hotmail.com

structure, and changes of the resistivity can reflect alteration of the mean free path, L_0, of conduction electrons and also the electron transport properties. In this study, the electrical resistivities, (ρ), of liquid Sn–Bi alloys have been measured continuously in several heating and cooling cycles in order to investigate the reversibility of LLT. The results show that the change of resistivity with temperature is obviously discontinuous both on heating and cooling in several experimental cycles, which indicates that there are reversible temperature-induced liquid–liquid transitions in Sn–Bi alloys. In addition, this kind of reversible LLT provides experimental evidence suggestive of LLT.

2 Experimental

In this study, the electrical resistivity measurements were carried out by the dc four-probe technology. The voltage was measured by a Keithley-2182 nanovoltmeter, while a constant current of 500 mA was supplied by a PF66M source meter. Measuring cells manufactured from silica glass, 3.38 mm in diameter, were used in this experiment. The thermal expansion of the silica glass was so small that variations of the measuring cell with temperature could be neglected. The experimental details and equipment have been described elsewhere [11].

According to the Sn–Bi phase diagram [12], Sn–Bi40 mass%, Sn–Bi57 mass%, and Sn–Bi70 mass% were selected for the measurements. Each sample was prepared from pure (99.9 mass%) tin and bismuth granules in a ceramic crucible using an electrical resistance furnace. All samples were melted at 500 °C for 30 min while covered with B_2O_3, and then poured into the measuring cells for the following experiments. The electrical resistivity measurements were carried out in purified argon media. The heating and cooling rates were set at $8\,^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$, $6\,^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$, and $4\,^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$ for the several experimental cycles.

3 Results and Discussion

The electrical resistivity of Sn–Bi40 mass%, Sn–Bi57 mass%, and Sn–Bi70 mass% samples versus temperature are shown in Figs. 1,2, and 3, respectively. As seen in the figures, reversible changes can be observed on resistivity–temperature (ρ–T) curves after the first heating cycle. The reversible changes on the ρ–T curves indicate that reversible liquid–liquid transitions probably take place in Sn–Bi alloys.

Comparing the character of the ρ–T curve for the first heating cycle with those of the subsequent cooling and heating cycles, we find that the turning points and the changes in trends of the resistivity are different, which indicates that the character of the LLT in Sn–Bi alloys in the first heating cycle is different from those of the subsequent cooling and heating cycles.

In addition, the resistivities of pure tin and bismuth have also been investigated, as shown in Figs. 4 and 5. For Sn, there are clear turning points both on heating and cooling in several experimental cycles. For Bi, a hump phenomenon is observed in the ρ–T curve during the first heating process, however, there is no anomalous change in the first cooling process and the second heating and cooling cycles. In other words,

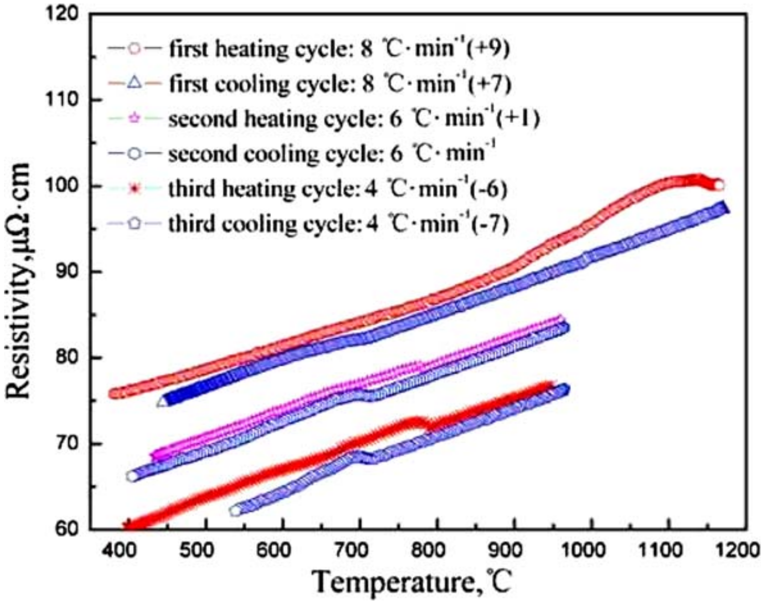

Fig. 1 Electrical resistivity–temperature curves of Sn–Bi40 mass% alloy for three heating and cooling cycles; positive or negative values in parentheses after each cycle signify the amount that the ordinate value has been moved to avoid overlap of curves

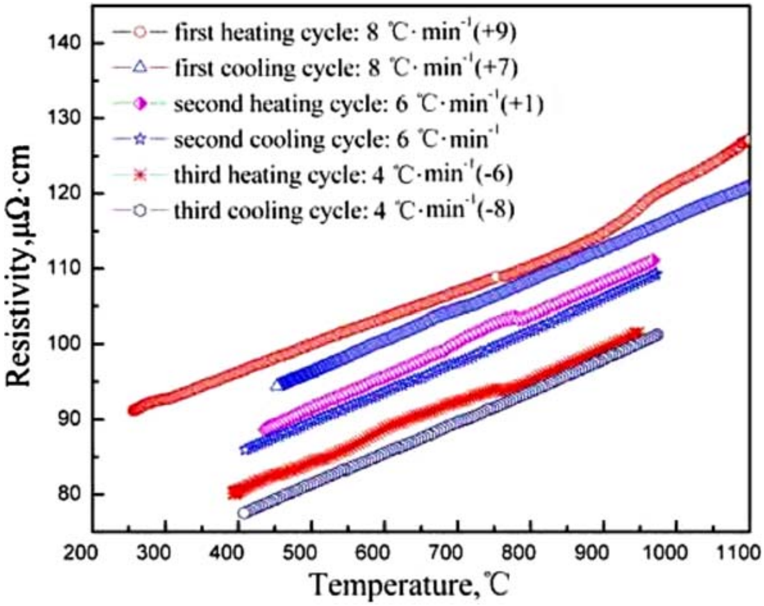

Fig. 2 Electrical resistivity–temperature curves of Sn–Bi57 mass% alloy for three heating and cooling cycles; see Fig. 1 for meaning of values in parentheses

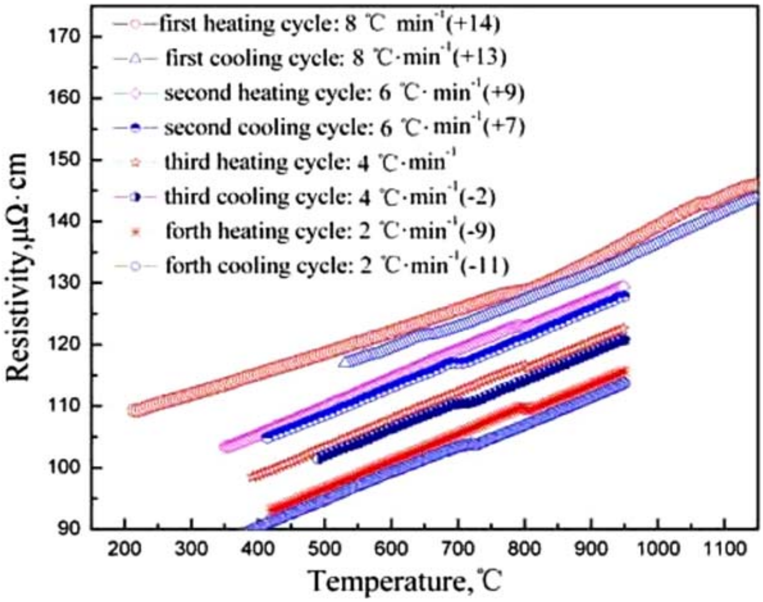

Fig. 3 Electrical resistivity–temperature curves of Sn–Bi70 mass% alloy for four heating and cooling cycles; see Fig. 1 for meaning of values in parentheses

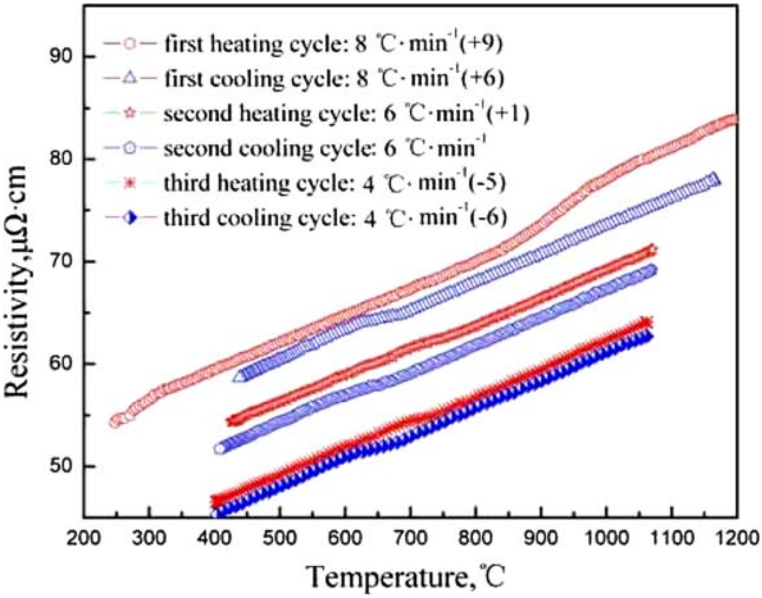

Fig. 4 Electrical resistivity–temperature curves of pure Sn for three heating and cooling cycles; see Fig. 1 for meaning of values in parentheses

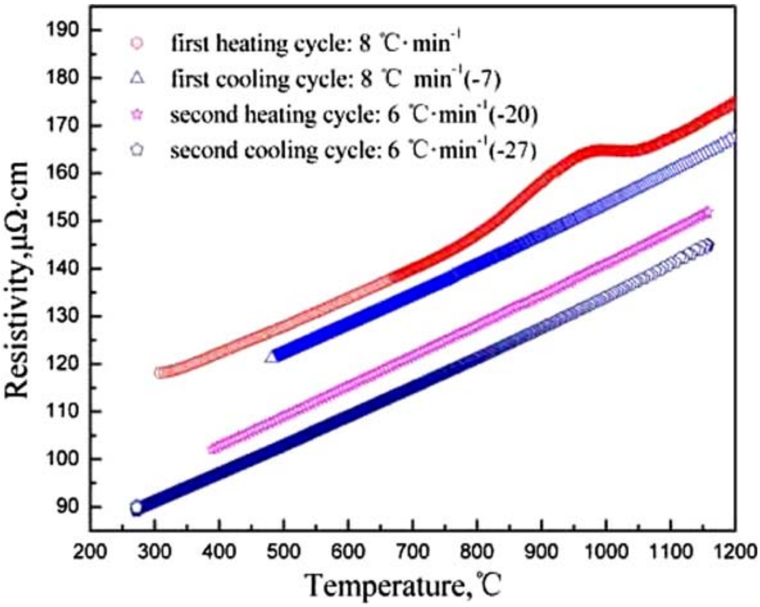

Fig. 5 Electrical resistivity–temperature curves of pure Bi for two heating and cooling cycles; see Fig. 1 for meaning of values in parentheses

the resistivity of Bi changes linearly with temperature after the first heating cycle. The above experimental results show that the LLT in liquid Sn is reversible. Comparing the LLT character of Sn–Bi melts with that of liquid Sn, the characteristics of these LLTs are quite similar, which reveals that Sn may play an important role in the reversible liquid–liquid transition in Sn–Bi melts.

In general, it may be accepted that the atomic bonds in crystals are only partly broken on melting and the short-range order (SRO), similar to the corresponding solid crystal, still remains in liquids [13–15]. It is known that the mutual solubility of Sn–Bi alloys is very small in the solid state, and there are probably still many Sn-rich or Bi-rich SROs in liquid Sn–Bi alloys at a low temperature above the liquids. And these Sn-rich or Bi-rich SROs are metastable. With increasing temperature, the metastable SRO will gradually change into a stable SRO. On the other hand, according to Ref. [16], neutron scattering experiments have been carried out to investigate the structure of liquid Sn. The experimental result shows that there is a clear shoulder on the high-Q side of the first peak of S(Q) at 573 K and 773 K, and even at 1873 K, such a shoulder may still be present. As is well known, the shoulder is a sign of a covalent bond. These features for liquid Sn indicate that some tetrahedral SROs with covalent characteristics may remain in liquid Sn at lower temperatures, and at least the fragments of tetrahedral units may persist even at high temperatures in liquid Sn [16,17]. Based on the results of neutron scattering experiments, we can assume that tetrahedral SROs with covalent characteristics in liquid Sn and Sn–Bi melts may be the main cause of the reversibility of liquid–liquid transitions.

As mentioned above, the structure transition in the first heating cycle is different from other cycles. The observation of irreversible changes in the Sn–Bi liquid suggest that the initial alloy during the first heating cycle was in the metastable state and the existence of large activation barriers between this state and an equilibrium one. This metastable state of the melt exists for long times which cannot be explained by any theory of liquids. Hence, one can suppose: there are some long-lived metastable clusters in the liquid in the first heating cycle which are not described by current theories. According to the results of electrical resistivity experiments, we can suggest that there are both reversible SROs and irreversible SROs in the first heating cycle in Sn–Bi melts. So, there may be two kinds of LLTs in the first cycle heating. One is the metastable-to-stable transition, the other is the reversible breaking and rebuilding of the covalent bond of tetrahedral SRO. As seen from the ρ–T curve in the first heating cycle, the metastable SRO is broken into stable SRO with increasing temperature, which will result in a rapid increase of the resistivity of the Sn–Bi melts; while when the temperature reaches a certain turning temperature, the covalent bonds of tetrahedral SRO of Sn break and release more free electrons, leading to a decrease or slow rise of the resistivity with temperature in the transition temperature range. After the first heating cycle, the short-range order derived from the corresponding crystal state (Sn-rich or Bi-rich SRO) break or dissolve into a more disordered structure. Only the tetrahedral SRO remains in the melts, which will break on heating and rebuild on cooling in the transition temperature range. This may be the reason why the transition in the first heating cycle is different from those of other cycles.

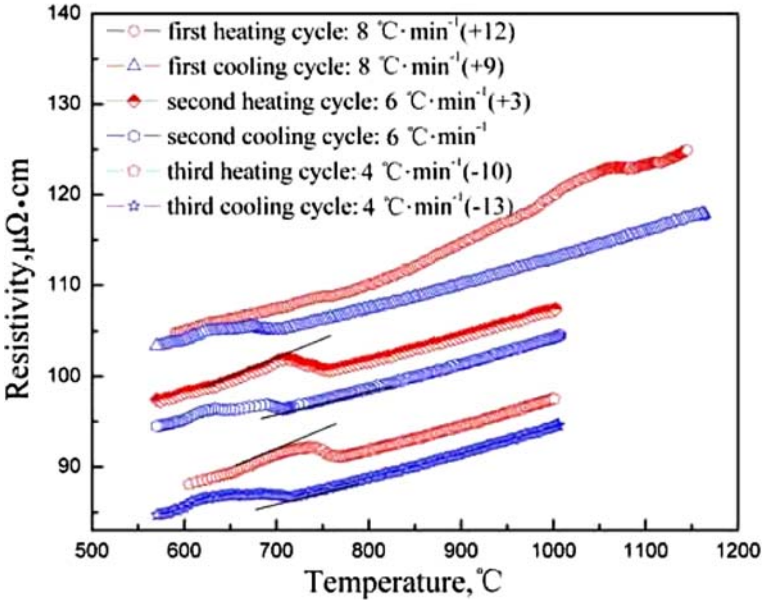

Fig. 6 Electrical resistivity–temperature curves of Sn-Sb80 mass% alloy for three heating and cooling cycles; see Fig. 1 for meaning of values in parentheses

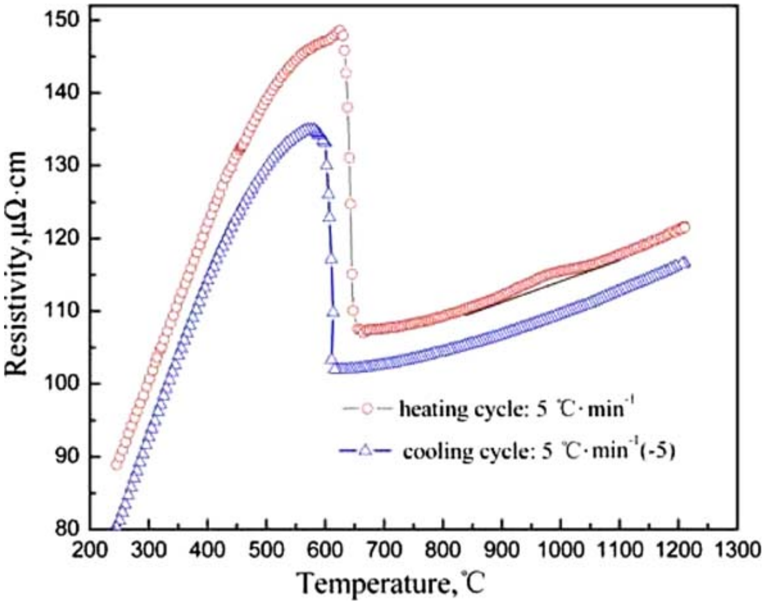

Fig. 7 Electrical resistivity–temperature curves of pure Sb; see Fig. 1 for meaning of values in parentheses

Although we postulate that Sn plays an important role in the reversible LLT of Sn–Bi melts, the reversible LLTs in Sn-rich (Sn–Bi40 mass%) and Bi-rich (Sn–Bi70 mass%) Sn–Bi melts are both evident, just the reversible LLT phenomenon in the eutectic composition Sn–Bi57 mass% on cooling is less obvious than that of the others. This phenomenon indicates that a different composition with various amounts and sizes of SRO also has some impact on the reversible LLT.

In order to further prove the effect of Sn on the reversibility and analyze the real existence of the reversible change, the electrical resistivity of Sn–Sb80 mass% and pure Sb are also investigated, the results are shown in Figs. 6 and 7. Comparing the ρ–T curves of Sn–Sb and Sn–Bi alloys with those of pure Sn, Bi, and Sb, the results show that Sn may play an active role in the reversible liquid-liquid transition in Sn alloys. At the same time, these results make the existence of a reversible liquid–liquid transition further convincing.

4 Conclusion

In summary, the electrical resistivity of Sn–Bi melts with different compositions has been measured, and anomalous variations of the resisitivity at certain temperature ranges are observed in several experimental cycles, which indicate that the possible temperature-induced liquid–liquid transition is reversible. A similar reversible change is also observed in liquid Sn, but is irreversible in liquid Bi.

The analysis indicates that, in liquid Sn or Sn–Bi melts, the tetrahedral Sn–Sn or Sn–Bi SRO with a characteristic covalent bond breaks on heating and rebuilds on subsequent cooling in the transition temperature range, which leads to the reversible change in Sn–Bi melts.

Acknowledgments This work was supported by the National Natural Science Foundation of China (No.50571033), and by the Natural Science Foundation of Anhui Province (No.070416234 and No.070414178).

References

1. Q. Wang, X.M. Chen, C.X. Li, K.Q. Lu, J. Appl. Phys. **87**, 4623 (2000)
2. Y.R. Wang, K.Q. Lu, C.X. Li, Phys. Rev. Lett. **79**, 3664 (1997)
3. F.Q. Zu, Z.-G. Zhu, L.-J. Guo, X.-B. Qin, H. Yang, Phys. Rev. Lett. **89**, 125505 (2002)
4. T. Gu, J. Qin, X. Bian, C. Xu, Y. Qi, Phys. Rev. B **70**, 245214 (2004)
5. V.V. Brazhkin, R.N. Voloshin, S.V. Popova, A.G. Umnov, Phys. Lett. A **154**, 413 (1991)
6. K. Tsuji, Y. Katayama, J. Non-Cryst. Solids **117–118**, 27 (1990)
7. M. Van Thiel, F.H. Ree, Phys. Rev. B **48**, 3591 (1993)
8. M. Togaya, Phys. Rev. Lett. **79**, 2474 (1997)
9. E.G. Ponyatovsky, I.O. Barkalov, Mater. Sci. Rep. **8**, 147 (1992)
10. P.H. Poole, T. Grande, C.A. Angell, P.E. McMillan, Science **275**, 322 (1997)
11. J. Yu, F.Q. Zu, H.F. Ding, L. J. Liu, X.F. Li, G.X. Xue, Chin. J. Rare Met. **28**(5), (2004)
12. H. Okamoto, T.B. Massalski (eds.), *Binary Alloy Phase Diagrams*, vol. 1 (ASM International, Metals Park, OH, 1990)
13. N.K.P. Singh, R.N. Singh, P.B. Choudhary, J. Phys. Condens. Matter **3**, 3635 (1991)
14. H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimaki, T. Lippamnn, G. Reiter, Nature **408**, 839 (2000)
15. W. van der Lugt, J. Phys. Condens. Matter **8**, 6115 (1996)
16. T. Itami, S. Munejiri, T. Masaki, H. Aoki, Y. Ishii, T. Kamiyama, Y. Senda, F. Shimojo, K. Hoshino, Phys. Rev. B **67**, 064201 (2003)
17. Y. Waseda, *The Structure of Non-crystalline Materials* (McGraw-Hill, New York, 1980), pp. 60–120