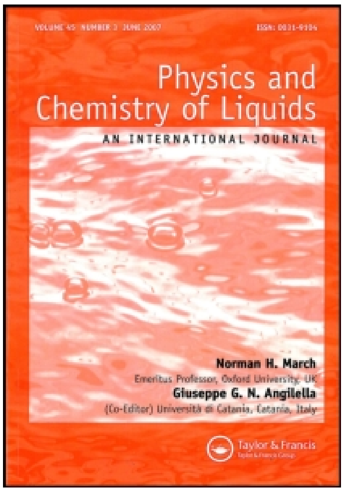

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Reversible resistivity-temperature anomalies of liquid Pb-Bi-Sn alloys

Xianfen Li[a]; Jigang Li[a]; Fangqiu Zu[a]; Chengming Hu[a]; Xun Yi[a]
[a] School of Materials Science and Engineering, Hefei University of Technology, Hefei, China

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Reversible resistivity–temperature anomalies of liquid Pb–Bi–Sn alloys

Xianfen Li*, Jigang Li, Fangqiu Zu, Chengming Hu and Xun Yi

School of Materials Science and Engineering, Hefei University of Technology, Hefei, China

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The patterns of electrical resistivity of (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys, along with liquid Pb–Bi56.1 wt% alloy and pure Pb, Sn and Bi have been investigated as a function of temperature, using the DC four-probe technique. Evident reversible changes are observed on resistivity–temperature curves of different liquid Pb–Bi–Sn alloys, and there are clear turning points both in the heating and cooling process, which are similar to that of liquid Sn. Moreover, the turning temperatures vary with differing compositions of alloys. In the case of the Pb–Bi alloy, however, no reversible changes are observed on resistivity–temperature curves. Since resistivity is one of the physical properties sensitive to structures, it is suggested that there are reversible temperature-induced liquid–liquid transitions in (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys, and that Sn plays an important role in the change.

Keywords: liquid Pb–Bi–Sn alloys; electrical resistivity; reversible liquid–liquid transition

PACS: 61.25Mv; 72.15Cz

1. Introduction

In recent years, the liquid–liquid transition (LLT) has been suggested experimentally and theoretically to occur in some one-component and a few multiple component systems [1–5]. Growing indications for first-order transitions in liquids have come from analysis of their physical properties and from computer simulations [6,7]. The occurrence of LLT has been demonstrated, or is at least strongly suggested to occur, within a wide range of chemical systems, such as chemical elements with bonding ranging from metallic to covalent, simple chemical compounds, multi-component mixtures and organic compounds [8]. According to the model proposed by Tanaka [9], LLT can, in principal, exist in any liquid in its stable, metastable or unstable state. With an internal friction method newly developed for liquids, temperature-induced discontinuous liquid structural changes at constant pressures have been put forward in some binary alloys, such as In–Sn, In–Bi, Pb–Sn and Pb–Bi far over the liquidus [10–13]. By the analysis of electrical resistivity and EXAFS [14–16], covalent bonds deriving from the solid state were found remaining in Sb-rich In–Sb melts and liquid antimony near the liquidus, which broke at a high temperature. From several studies [14–19], chemical short-range orders (CSROs) corresponding to the crystal structures have been proved to remain in some single and/or multi-component liquids at the temperature near liquidus, besides the topological SROs.

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*Corresponding author. Email: lxfytt@163.com

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Although there are numerous experimental indications suggestive of LLT existence [6], such a transition seems not to have been widely accepted as a convincing fact, and its existence itself is still a matter of debate [20]. This situation comes partly from experimental difficulties, and partly from the irreversibility of the LLT. However, the infusive findings of first-order LLT in P [21] and the reversible LLT in the molecular liquid triphenyl phosphite [20] makes its existence more convincing. The reversibility might be regarded as a reliable evidence of LLT. Although there were some investigations of LLT on liquid Sn, Bi, and others under high temperature and high pressure conditions [22,23], to our knowledge, there are scarcely any up-to-date investigations and reports on the reversibility of temperature-induced LLT in liquid metals and alloys at high temperature. In this article, the electrical resistivities (ρ) of liquid $(\mathrm{Pb{-}Bi56.1})_{1-x}{-}\mathrm{Sn}_x$ alloys have been investigated as a function of temperature, and they have been measured continuously in several heating and cooling cycles in order to probe the reversibility of the transition. At the same time, the Pb–Bi56.1 wt% alloy, as well as pure Sn, Pb and Bi were also investigated to be compared with the $(\mathrm{Pb{-}Bi56.1})_{1-x}{-}\mathrm{Sn}_x$ alloys, in order to explore the nature of the transition.

2. Experiments

According to Pb–Bi phase diagram [24], the eutectic Pb–Bi56.1wt% was chosen as the referenced alloy; different amounts of Sn were added to form different $(\mathrm{Pb{-}Bi56.1})_{1-x}{-}\mathrm{Sn}_x$ alloys. In this article, four compositions of Pb–Bi–Sn alloy were chosen for the ρ–T experiments, that is, (Pb–Bi56.1)–Sn20, (Pb–Bi56.1)–Sn40, (Pb–Bi56.1)–Sn60 and (Pb–Bi56.1)–Sn80 wt%. All the Pb–Bi–Sn samples were prepared with pure Pb, Sn and Bi granules of 99.99% purity. After melted and held at a temperature of 500°C for 30 min, the melts were poured into quartz cells for the following experiments. In order to minimise the deviation of the cell size, the cells were made of quartz, which has a relatively small thermal expansion.

The electrical resistivities were measured by the DC four-probe method, and the quartz cell was placed in the homogeneous heat area of the furnace to eliminate as much thermal EMF (electromotive force) as possible. Furthermore, the DC current-reversal technique was used to cancel any thermal EMFs which may occur with the connection points and temperature fluctuations in the test leads [25], and the resistivities have been measured continuously in several heating and cooling cycles in the liquid state in order to probe the reversibility of LLT; the heating and cooling rates were set as 7.5, 5, 10 and 2°C min^{-1} in different cycles. The potential drop was measured by a KEITHLEY-2182 nanovoltmeter with a PF66M current source providing the constant current. Tungsten wires with a diameter of 1 mm were employed as current and potential electrodes. The whole measuring process was under the shield of argon gas.

3. Results and discussions

The resistivity of the Pb–Bi56.1 wt% alloy *versus* temperature is shown in Figure 1. In the first heating process, an evident turning point is observed in the resistivity–temperature curve; however, there is no turning point in the first cooling process nor the second heating and cooling cycles. In other words, the resistivity of the Pb–Bi56.1 wt% alloy changes evenly with various temperatures after the first heating cycle. According to the results of

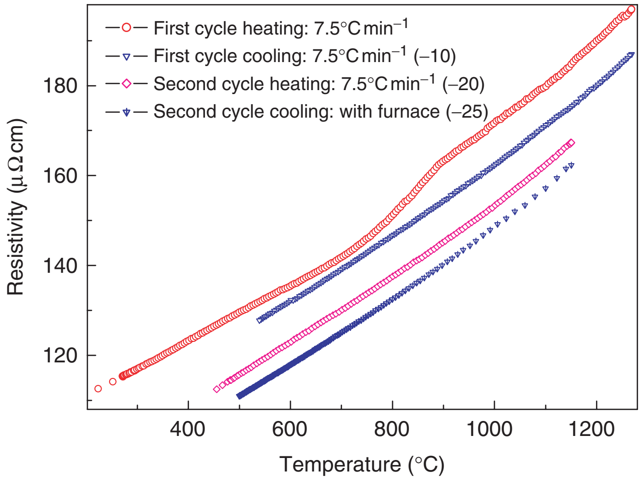

Figure 1. The resistivity–temperature curves of the Pb–Bi56.1 wt% alloy in two heating and cooling cycles (colour online).

the electrical resistivity experiment, it is assumed that the possible LLT during the first heating process is irreversible in liquid Pb–Bi56.1 wt% alloy during the subsequent cooling and heating process.

The resistivity–temperature curves of the (Pb–Bi56.1)$_{60}$–Sn$_{40}$ alloy shown in Figure 2 are different from that of the Pb–Bi56.1 wt% alloy: visible and reversible changes are observed on resistivity–temperature curves of (Pb–Bi56.1)$_{60}$–Sn$_{40}$ in four heating and cooling cycles; that is to say, there are clear turning points both in the heating and cooling processes. Further, the turning points are hundreds of degrees above the liquidus: the turning temperature difference between heating and cooling is due to the hysteresis effect of transition. Also, we can see similar reversible changes of different cycles in the resistivity–temperature curves of (Pb–Bi56.1)$_{20}$–Sn$_{80}$, (Pb–Bi56.1)$_{40}$–Sn$_{60}$ and (Pb–Bi56.1)$_{80}$–Sn$_{20}$ alloys, as shown in Figure 3. The anomalous change of resistivity with temperature indicates that LLTs may exist in liquid (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys, and the LLT is reversible after the first cycle heating. Referring to the irreversible LLT in the Pb–Bi56.1 alloy, we presume that the reversible LLTs in liquid (Pb–Bi56.1)$_{1-x}$–Sn$_\mathrm{x}$ alloys may mainly be attributed to Sn. Accordingly, the electrical resistivities of liquid Sn, Pb and Bi were measured at similar conditions as those of the ternary alloys, and the results are shown in Figure 4. From Figure 4, the reversible changes of the resistivity–temperature curves can only be observed in liquid Sn, whose transition characteristic is consistent with that of (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys, which indicates the reversible transition of (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys may be caused by Sn.

It should be pointed out that the character of LLT in (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys in the first heating cycle is different from that of the subsequent cooling and heating cycles, as shown in Figure 2(a). After the first cycle heating process, the LLT in the (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloy presents reversibility. Moreover, as seen in Figure 2, heating and cooling rates affect the transition: namely, the LLT is more obvious during slower heating. While comparing the corresponding transition point in second heating cycle (5°C min^{-1}) with that of the fourth heating cycle (2°C min^{-1}), as labelled in Figure 2(b),

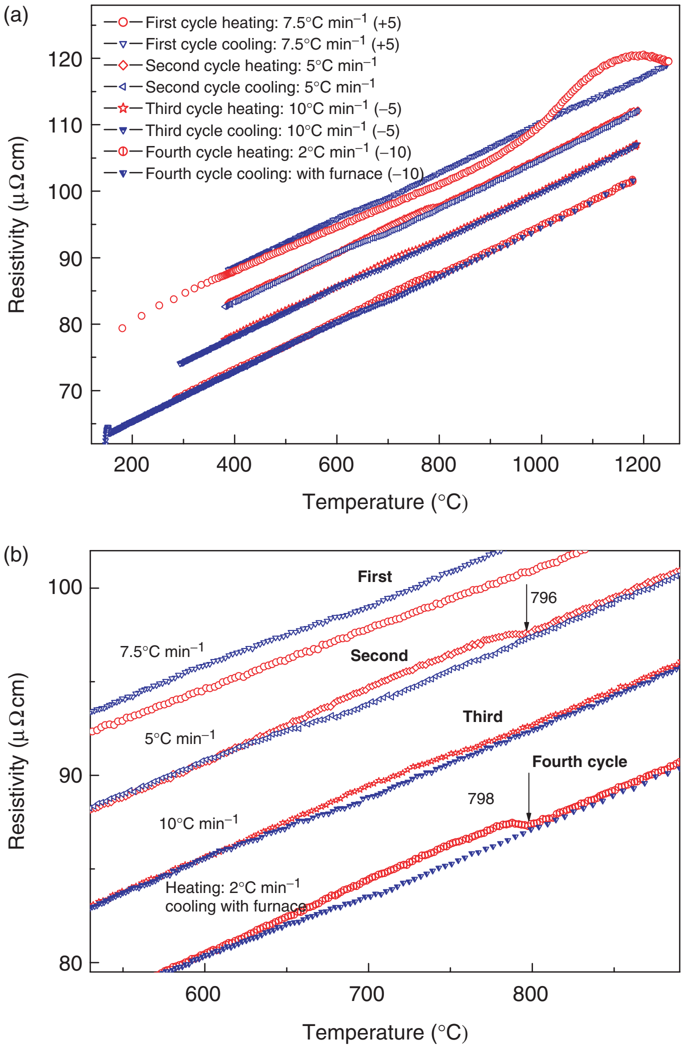

Figure 2. The resistivity–temperature curves of the (Pb–Bi56.1)$_{60}$–Sn$_{40}$ alloy in four heating and cooling cycles. (a) Resistivity–temperature curves of the (Pb–Bi56.1)$_{60}$–Sn$_{40}$ alloy. (b) Local amplification of (a) (colour online).

the temperature difference between the two points is small, which indicates the heating rate hardly affects the reversible transition temperature during heating.

It is generally agreed that the atomic bonds of crystals are only partly broken on melting, and there are lots of minor short-range ordering domains in the melts, around which there are mass free atoms. It is reasonable to assume that when the alloys are heated to the turning point in the first heating process, the remaining Sn–Sn, Bi–Bi, Sn–Bi, Pb–Sn, etc. SROs (similar to crystal) are broken; at the same time, a new liquid structure builds up, which is maintained steadily in the succeeding heating process. After the transition in the first heating cycle, the liquid alloys reach a stable homogeneous state. Comparing the

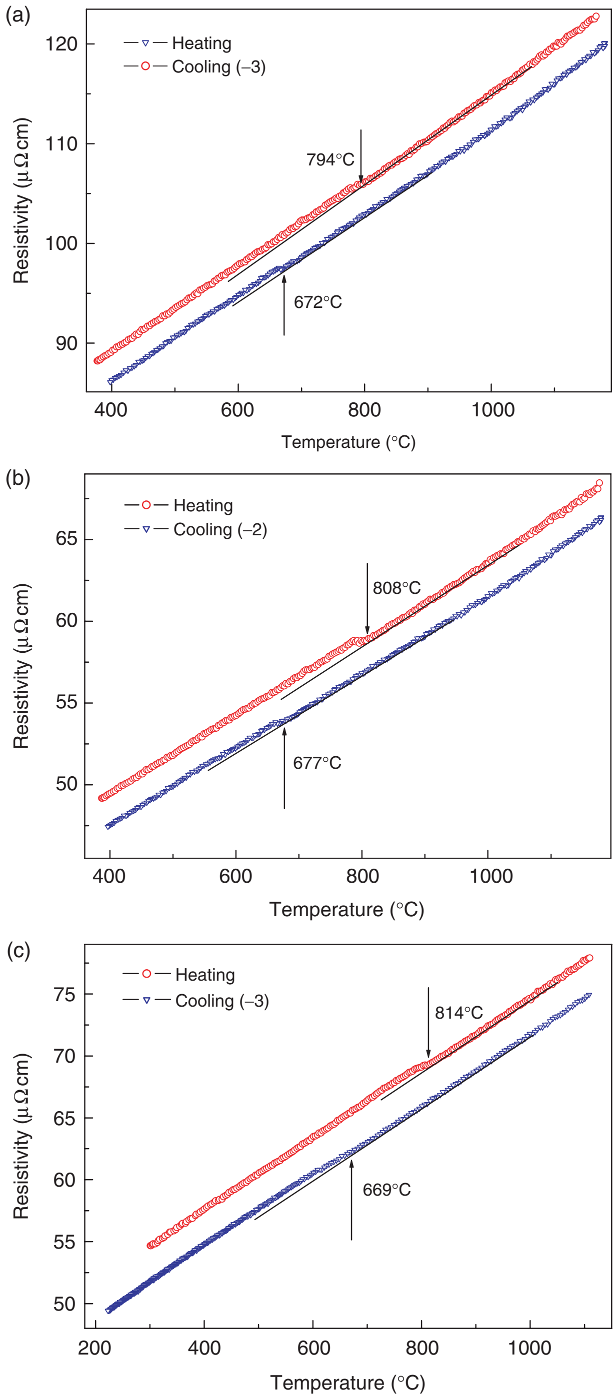

Figure 3. The resistivity–temperature curves of (Pb–Bi56.1)$_{1-x}$–Sn$_x$ alloys. (a) (Pb–Bi56.1)$_{80}$–Sn$_{20}$ in the third heating and cooling cycle (2°C min^{-1}). (b) (Pb–Bi56.1)$_{40}$–Sn$_{60}$ in the third heating and cooling cycle (2°C min^{-1}). (c) (Pb–Bi56.1)$_{20}$–Sn$_{80}$ in the second heating and cooling cycle (5°C min^{-1}) (colour online).

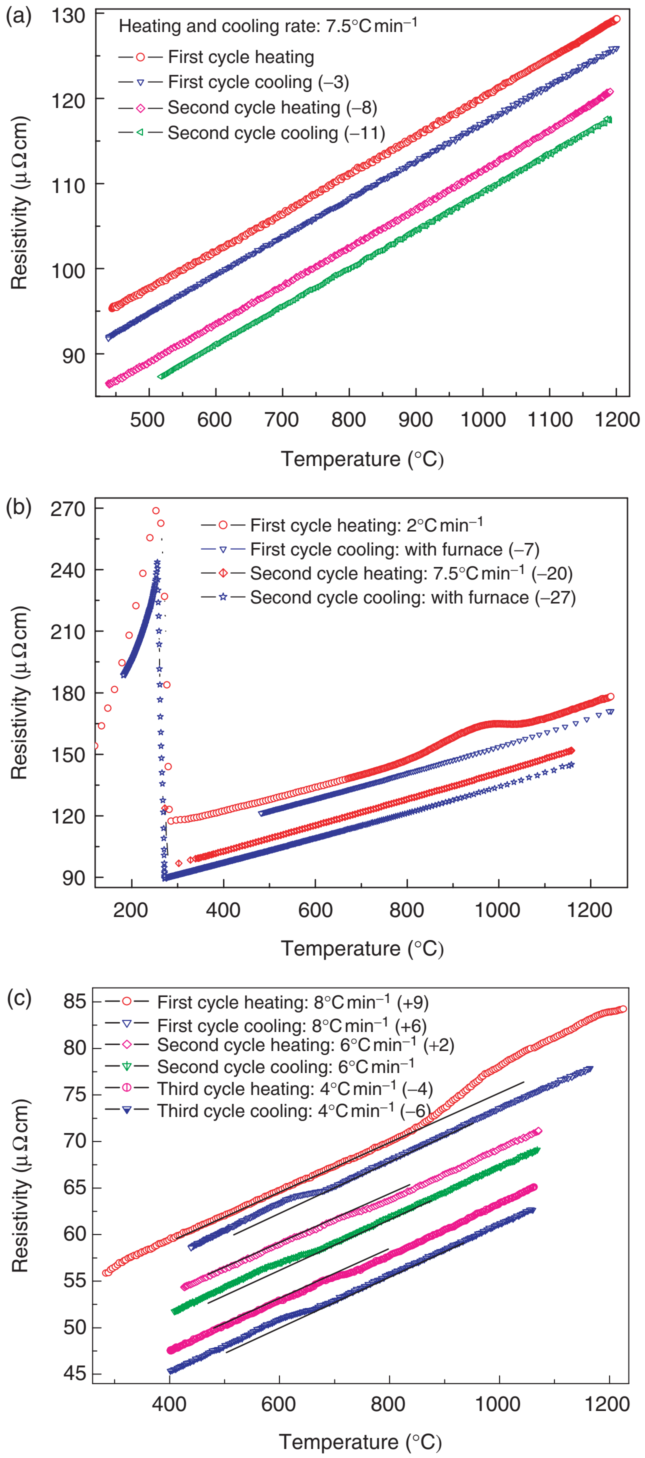

Figure 4. The resistivity–temperature curves of pure metals in two heating and cooling cycles: (a) pure Pb, (b) pure Bi, (c) pure Sn (colour online).

character of the resistivity–temperature curve in first heating cycle with that of the subsequent cooling or heating cycles (as seen in Figure 2), we can assume that the LLT in the first heating cycle may include inhomogeneous to homogenous transition (irreversible) and reversible LLT, and the inhomogeneous to homogenous transition plays a dominant role, while the part of reversible LLT is hidden behind. Comparing the resistivity–temperature curves of $(\text{Pb–Bi56.1})_{1-x}$–Sn_x alloys with those of the Pb–Bi56.1 wt% alloy and liquid Sn, Bi, Pb, it is reasonable to suppose that Sn plays an important part in the formation of the reversible structure: namely, when the alloys are cooled to the turning temperature in the cooling process, new Sn–X tetrahedral SROs with covalent characteristics [26] (including Sn–Sn, Sn–Bi, Sn–Pb) build up; however, in the heating process, when the temperature reaches the turning point, Sn–X SROs with covalent characteristics are broken again to release more free electrons, which influence the changing slope of the resistivity–temperature curves during the transition. This may be the reason that there are reversible transitions in Pb–Bi–Sn alloys while the change is irreversible in liquid Pb–Bi alloys.

In addition, the resistivity–temperature curves of different Pb–Bi–Sn melts turn at various temperatures during heating, which become higher with the increasing of Sn wt%, as shown by the labelled numbers in Figures 2 and 3. In a heating process of $2\,\text{min}^{-1}$, the turning point of the resistivity–temperature curves can be found at 794 for (Pb–Bi56.1)–Sn20 wt% in the third heating cycle, at 798 for (Pb–Bi56.1)–Sn40 wt% in the fourth heating cycle, and at 808 for (Pb–Bi56.1)–Sn60 wt% in the third heating cycle. Taking the different turning points with composition into account, we take it for granted that the amount of Sn–Sn, Sn–Bi, Pb–Sn SROs has some effect on the turning temperature.

4. Conclusions

In summary, the patterns of electrical resistivity *versus* temperature of $(\text{Pb–Bi56.1})_{1-x}$–Sn_x alloys have been investigated as a function of temperature in the present article, and evident reversible LLTs are observed from the resistivity–temperature curves of these alloys.

The turning points on the resistivity–temperature curves indicate the temperature dependence of LLTs may occur in liquid $(\text{Pb–Bi56.1})_{1-x}$–Sn_x alloys at temperatures far above their liquidus. The SROs derived from the corresponding crystal state begin to break up or dissolve into a more disordered structure at this temperature, which causes the unusual change of the resistivity in liquid $(\text{Pb–Bi56.1})_{1-x}$–Sn_x alloys in the first heating cycle. New, stable reversible structures may be obtained after the first heating cycle, which causes the reversible change on the resistivity–temperature curve, and Sn plays an important role in the formation of the reversible bonds. Moreover, the reversible transition in liquid Pb–Bi–Sn alloys might supply evidence for the existence of LLTs in liquid metals and alloys.

Acknowledgements

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