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Electrical resistivity of liquid Sn–Sb alloy

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Abstract

An investigation of the temperature dependence of the electrical resistivity (ρ–T) of Sn–Sb alloys is carried out, using the DC four-probe method. A clear turning point is observed in some compositions of the Sn–Sb melt, but not at every composition, at which the resistivity–temperature coefficient increases rapidly. The anomalous variation of the resistivity at certain temperatures for the Sn–Sb melt may be due to the remaining covalent and heterogeneous bonds and also the difference in bonding ability between Sn and Sb atoms, which might yield temperature-induced structure changes in some compositions of liquid Sn–Sb alloys. Besides this, analysis of the composition dependence of the resistivity is also included in this paper.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Liquid alloys of noble metals with polyvalent elements are known to show non-linear concentration dependences of their physical properties. For example, they exhibit a considerable exothermic heat of mixing, increase of density, and maximum in diamagnetic susceptibility or electrical resistivity at some particular concentrations [1]. It is clear that the peculiar variations of the physical properties with composition of liquid alloys are basically caused by changes in their electronic and/or atomic structure, like those of solids. It seems to be becoming evident that many structural features and physical properties of liquid metals and alloys can be reasonably explained only under the assumption of microheterogeneous structure [2].

Sb-based alloys are the subjects 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 has been

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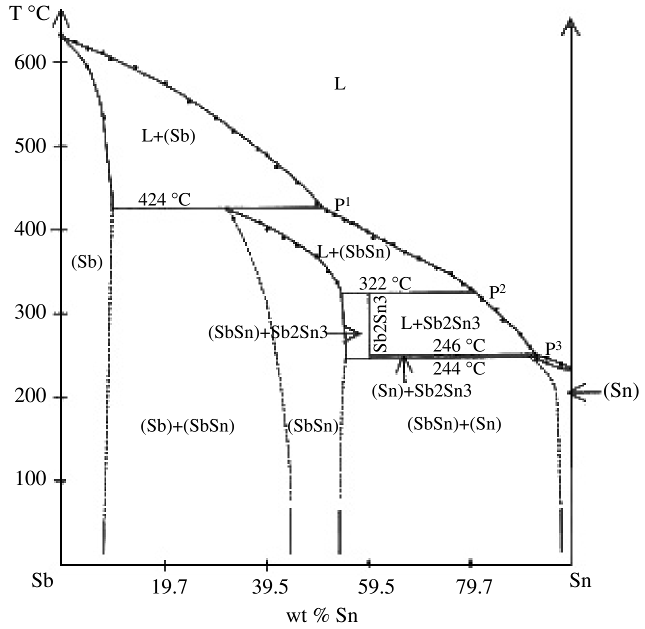


Figure 1. [20] Phase diagram of the antimony–tin system (at.% Sn is changed to wt% Sn).

reported [3]. When melting, Sb still retains the features of a semimetal, resulting in abnormal behaviour of the resistivity for pure antimony [4–10]. With the methods of electrical resistivity and EXAFS [11–13], covalent bonds deriving from solid states were found retained in Sb-rich In–Sb melts and liquid antimony, and then they broke at high temperature. Experimental data on the structural factors of Sb demonstrate that the low symmetry of the solid phase has a residual effect on the melt structure [14].

However, papers on Sn–Sb alloys [15–19] seldom concentrate on temperature-induced structural behaviour of Sn–Sb melts. Moreover, according to Sn–Sb phase diagram (figure 1 [20]), there are two intermediate phases and extended solid solutions. So it is interesting to make clear the effect of different phases on the resistivity in Sn–Sb melts. In this paper, we carry out an investigation of the temperature dependence of the electrical resistivity (ρ–T) and an analysis of the composition dependence of the resistivity of liquid Sn–Sb melts. It is assumed that the remaining covalent and heterogeneous bonds may have some effects on the abnormal behaviour of the Sn–Sb melt.

2. Experimental details

The electrical resistivity measurements were carried out by the DC four-probe method. The samples were prepared from 99.99% pure antimony and tin, which were melted at 650 °C for over 30 min, then poured into measuring cells before cooling down to room temperature for the following experiment. 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 the variation of the measuring cell with temperature could be neglected.

Four tungsten electrodes, 1 mm in diameter, two for current and two for voltage, were placed in the wall of the cell. The voltage was measured with a KEITHLEY-2182

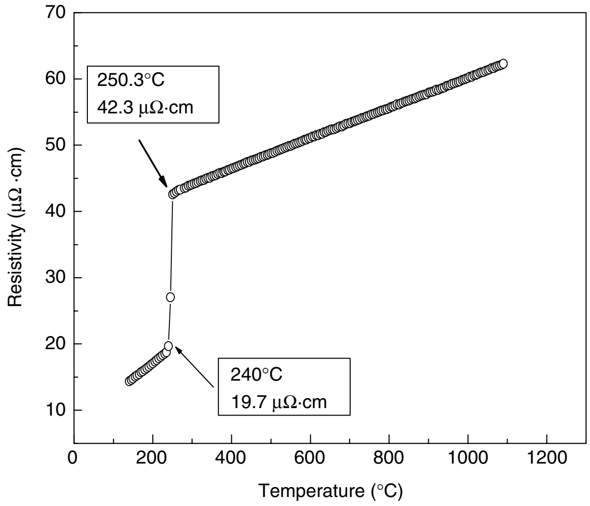


Figure 2. The resistivity–temperature curve of pure tin.

nanovoltmeter, while a constant current of 500 mA was supplied by the PF66M sourcemeter. The experimental details and equipment have been described elsewhere [21]. The resistivity measurements were carried out in purified argon media to protect the sample from oxidation. In each experimental series, we studied the temperature dependence of the electrical resistivity (TDR) of the samples by heating both at the rate of 5 °C min^{-1}. By repeating the measurements, we obtained a reproducible set of data, the experimental error of which is within 3%.

3. Results

The electrical resistivity was measured in Sb–Sn liquid alloy with 10, 30, 42, 50, 70 wt% antimony, on the basis of the Sn–Sb phase diagram.

Figure 2 shows the resistivity of tin versus temperature, in which the resistivity of pure Sn increases linearly with temperature elevated before and after the melting point (T_m), while it rises abruptly at T_m. In figure 3, we show the resistivity behaviour of pure Sb, showing the non-linear relation between resistivity and temperature above T_m.

Resistivity–temperature (ρ–T) curves of five Sb–Sn melts with different compositions are presented in figure 4. Different behaviours of the resistivity are observed for alloys with different compositions. In figures 4(a) and (b), non-linear behaviour is observed at relatively high temperature while the resistivity changes almost linearly with temperature elevation in the low temperature range, with a totally different transition mode. In addition, the curve of resistivity–temperature coefficients $\mathrm{d}\rho/\mathrm{d}T$–$T$ (temperature) is placed in the left top corner to provide a clearer picture of the abnormal behaviour of the Sn–Sb alloy. A great change, i.e. a sharp peak, is found in the curves of $\mathrm{d}\rho/\mathrm{d}T$–$T$ that indicates the changing rate of resistivity. The temperature at which the sharp peak occurs is defined as T_0 (the transition temperature). For Sn–10% Sb, T_0 is about 856 °C, while for Sn–30% Sb, the transition mode is changed after 876 °C.

Non-linear but continuous resistivity behaviour with temperature elevation is observed in Sn–42% Sb, which show completely different modes of resistivity in figures 4(a) and (b). Both

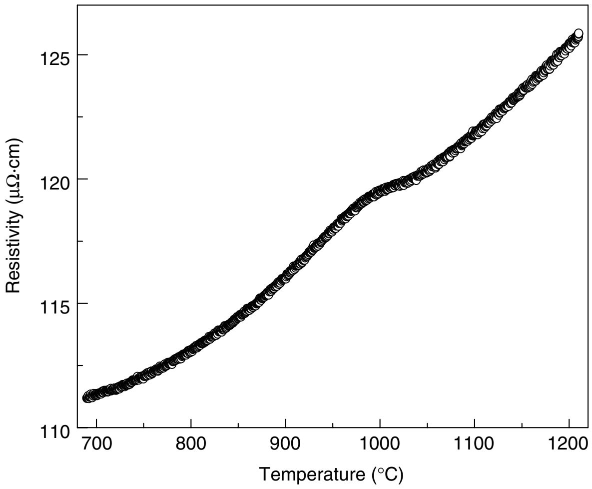


Figure 3. The resistivity–temperature curve of pure antimony.

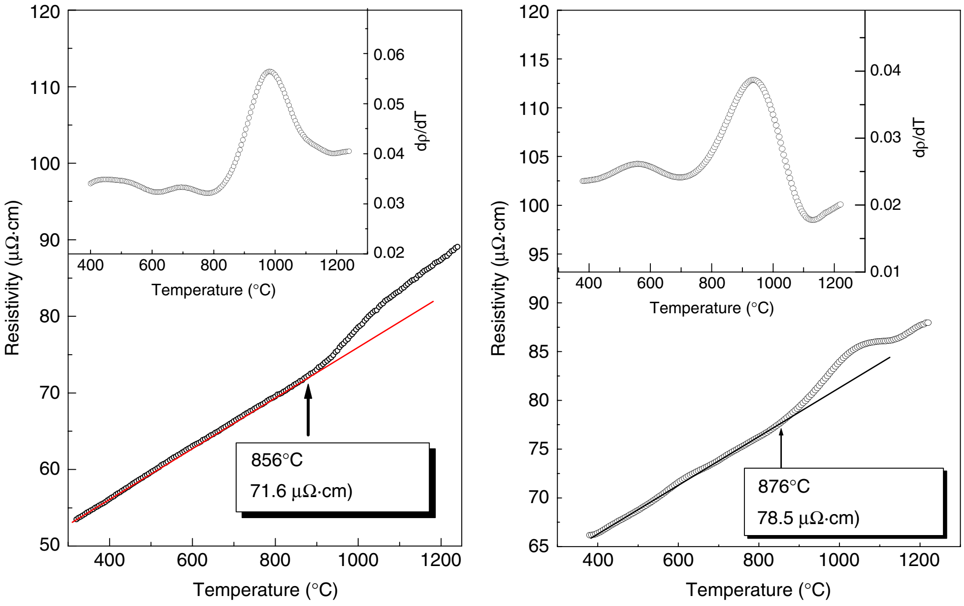
heating and cooling processes are plotted in figure 4(c), which coincide with each other. For Sn–50% Sb and Sn–70% Sb, the heating curves of the resistivity dependence of the temperature are shown in figure 4(d). Nearly the same behaviours of the resistivity are observed for these two compositions of alloy and Sn–42% Sb.

Besides this, in order to establish the dependence of the resistivity on the composition in this melt, we have plotted the relation between the resistivity and Sb content at several constant temperatures in figure 5.

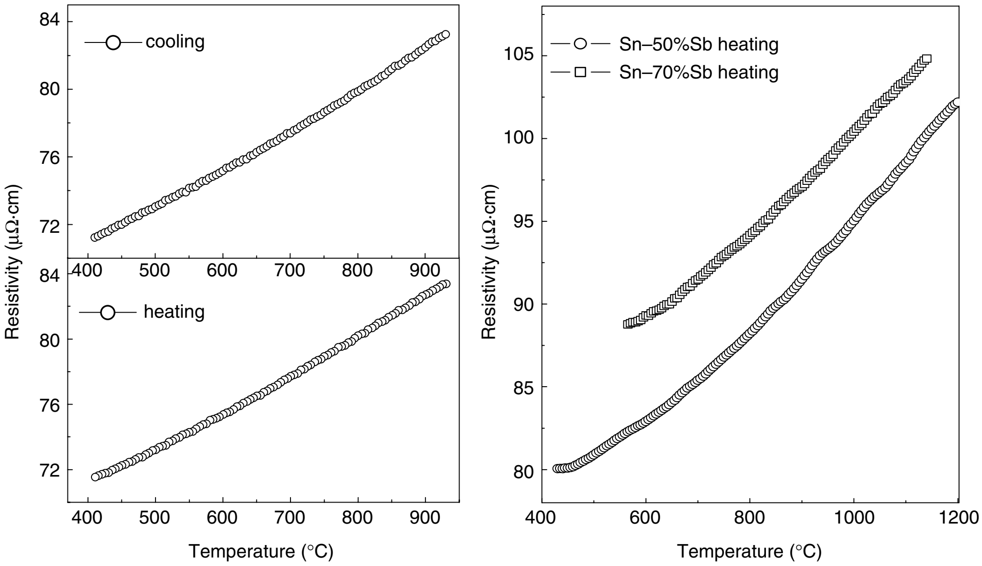
4. Discussion

Since the electron mean free path is shorter when the electrons are moving through disordered liquids, the increase of electrical resistivity in liquid tin is to be expected [22]. However, the non-linear behaviour in liquid antimony might be attributed to the fact that atom clusters $(\mathrm{Sb})_n$ with covalent bonds exist in liquid Sb at relatively low temperature with Sb atoms in random distributions [23, 24]. With temperature elevating, the metastable $(\mathrm{Sb})_n$ disappear completely. Namely, the existence of short range ordering (SRO) results in the abnormal behaviour of the resistivity for pure Sb.

Concerning alloys with 10% and 30% Sb, the sharp peak after T_0 is suggested to indicate a structural transformation in the relatively high temperature zone. The unusual change of resistivity may reflect an alteration in mean free path L_0 of the conduction electrons and also electron transport properties. Namely, the distance change among atoms and the altering of the bonding style are reflected. However, with increase of the Sb content in the alloy, a discontinuous change of resistivity does not occur in $\mathrm{Sn}_{1-x}\mathrm{Sb}_x$ $(x = 42, 50, 70)$, which is different from the case for other binary alloys, such as Pb–Sn, In–Bi [21, 25]. It could be seen from the phase diagram that in Sn-rich alloys, the metallic compound $(\mathrm{Sb_2Sn_3})$ exists, which would release a large quantity of free electrons when the metallic bond was broken at high temperature. Therefore, the resistivity of the melt increases sharply. While in the Sb-rich melt, more covalent bonds are broken, this is not so for metallic bonds, resulting in fewer free electrons. It is known that for Sb-based alloy, the smaller the difference in atom radius of the components, the lower the sensitivity of the atom clusters of Sb to the alteration of the alloy



(a) Sn-10%Sb (b) Sn-30%Sb



(c) Sn-42%Sb (d) Sn-50%Sb, Sn-70%Sb

Figure 4. Resistivity versus temperature for liquid Sn–Sb.

concentration. The behaviour of l-SnSb may correspond to microstructural changes at certain temperatures.

From figure 5, it is observed that resistivity rises with increase of the Sb content, since the resistivity of tin is far less than that of pure antimony. In the Sn/Sb-rich melt, free Sn/Sb atoms play an important role. We could see that for the composition range between Sn–42% Sb and

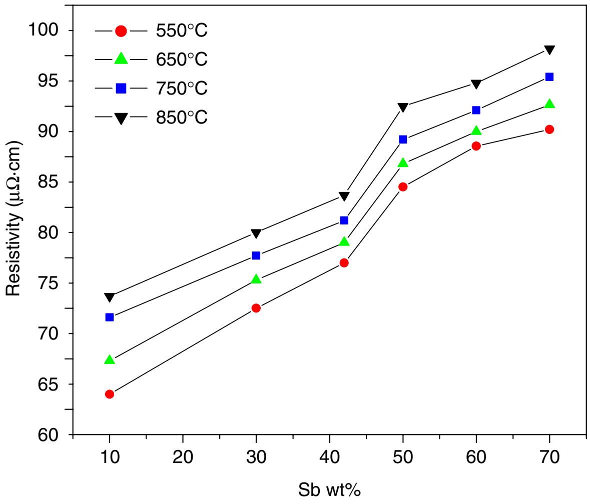


Figure 5. Resistivity versus composition at different temperatures.

Sn–50% Sb, the resistivity increases sharply compared with those for other compositions. It can be seen from figure 1 that in this composition range, the monophase (SbSn) exists.

5. Conclusion

The anomalous variation of the resistivity at certain temperatures for Sn–Sb melt may be due to the remaining covalent and heterogeneous bonds. It is also suggested that this could be a result of the structural change with temperature and the difference in bonding ability of Sn and Sb atoms.

Acknowledgments

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