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Jin Yu^a; Yan Zhang^a; Fang-Qiu Zu^a; Yun Xi^a; Xian-Fen Li^a; Wei Xu^a; Hai-Ming Liu^a

^a College of Materials Science and Engineering, Heifei University of Technology, Heifei Anhui province, People's Republic of China

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The abnormal changes of electrical resistivity in liquid Pb–In alloys

JIN YU, YAN ZHANG, FANG-QIU ZU*, YUN XI, XIAN-FEN LI,
WEI XU and HAI-MING LIU

College of Materials Science and Engineering, Heifei University of Technology,
Tunxi Road, Heifei Anhui province, 23009, People's Republic of China

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Electrical resistivity of liquid lead and indium (Pb–In) alloys with different compositions has been measured using the four-probe method in a large temperature range. Marked turning points on each resistivity–temperature (ρ – T) curve of the liquid Pb–In alloys can be observed far above the liquidus. The unusual variation of the resistivity of Pb–In melts suggests a structural transition of these melts, for resistivity is a sensitive parameter to the structure. Moreover, the DSC experiment of Pb–In melts supports the existence of a liquid–liquid (L–L) structure transition in Pb–In melts. Such a L–L structural transition can be described in terms of the gradual disappearance of atomic bonds corresponding to the crystal structure and/or to a reduction of the size of pre-formed atomic clusters. This implies an increase of disorder in the high temperature melts. The transition temperatures depend on the composition of Pb–In melts and the onset transition temperatures of the intermediate phase (α) Pb–63%In and Pb–70.6%In melts are higher than that of other compositions.

Keywords: Pb–In melts; Electrical resistivity; Structure transition

PACS: 72.15. Cz; 71.20. Gj

1. Introduction

Over the last decades, much attention has been paid to the experimental and theoretical investigation of the liquid–liquid (L–L) structural changes. Such studies have great prospects for applications and will help understanding the nature of L–L structural changes. It has been gradually accepted that the liquid phase lacks the same long-range order as in crystals but is not as disordered as the gaseous phase. Many methods have been used to prove that some short-range ordered structures (SROs) or clusters corresponding to the crystal structures still remain present in the liquid phase at temperatures near the liquidus. These include X-ray diffraction experiments, molecular

*Corresponding author. Tel.: +86-0551-2905057. Email: fangqiu@hotmail.com

dynamic simulations etc. [1–15]. There is growing experimental evidence showing that phase or structural transitions exist in some single and multi-component liquids as a function of temperature or pressure. For example, Katayama *et al.* [16] reported a reversible pressure-induced structural change of black P, using synchrotron X-ray diffraction; moreover, with internal friction method, electrical resistivity method, X-ray diffraction etc., the temperature-induced discontinuous liquid structural changes at a constant pressure have also been proved in some binary alloys, such as In–Sn, In–Bi, Pb–Sn and Pb–Bi far above the liquidus [17–22].

The alloys of lead and indium (Pb–In) are widely used as contact alloys for metal-glass or metal-ceramics connections because of their low melting temperatures. Therefore, it is interesting to investigate the properties of Pb–In melts. Elemental Pb and In are not easy to volatilize, so the data obtained at high temperatures are sufficiently realistic. To our knowledge, to date there has been no report on the liquid property of Pb–In alloys. Therefore, this study focuses on some electrical transport properties of Pb–In alloys.

In this article, the electrical resistivities (ρ) of pure Pb, In and liquid Pb–In alloys for five different compositions have been investigated in order to explore possible structural changes with temperature. The experimental results show that unusual variations occur on the resistivity–temperature (ρ – T) curves of these five liquid Pb–In alloys at temperatures far above the liquidus. These variations suggest that some local SROs or meta-stable atomic bonds maintaining in the molten state begin to disappear gradually at the onset temperature of the ρ – T curves. However, after the abnormal transition, ρ increase linearly with T again, which shows that such structural transition is completed and the liquid is steady and homogeneous at the microscopic scale. The sharp thermal absorption peak in DSC curve of Pb–In melts at high temperature also proves the existence of a L–L structural transition. This article also discusses the reasons why the turning points are different with different compositions and why the intermediate phase compositions have higher transition temperatures.

2. Experiment

High purity lumps of Pb (99.99%) and In (99.993%) were used as starting materials. According to Pb–In phase diagram [23], Pb–In (20 wt%), Pb–In (40 wt%), Pb–In (63 wt%), Pb–In (70.6 wt%) and Pb–In (89.75 wt%) were subjected to the experiment in this study. In addition, pure Pb and In were also studied for comparison with Pb–In alloys. After melting for 30 min, the melts were poured into quartz cells and cooled to room temperature for the following experiments. The thermal expansion of the silica glass is relatively small, so the variation of the cell size with temperature can be neglected.

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 thermal electromotive force (EMF) as much as possible. Furthermore, the DC current-reversal technique was used to cancel the thermal EMFs, which may be brought with the connection points and temperature fluctuations in the test leads [24]. During testing, the heating rate was set at $5^{\circ}\text{C min}^{-1}$. The potential drop was measured by a KEITHLEY-2182 nanovoltmeter with the Pf66M current source providing constant current.

Tungsten wires with a diameter of 1 mm were employed as current and potential electrodes. In order to avoid the rapid oxidation of the alloys, the whole experiments have been performed under the protection of purified argon.

3. Results and discussion

The resistivity (ρ) of pure Pb and In *versus* temperature is shown in figures 1 and 2, respectively. As the samples melt, the ρ of pure Pb and In increase remarkably

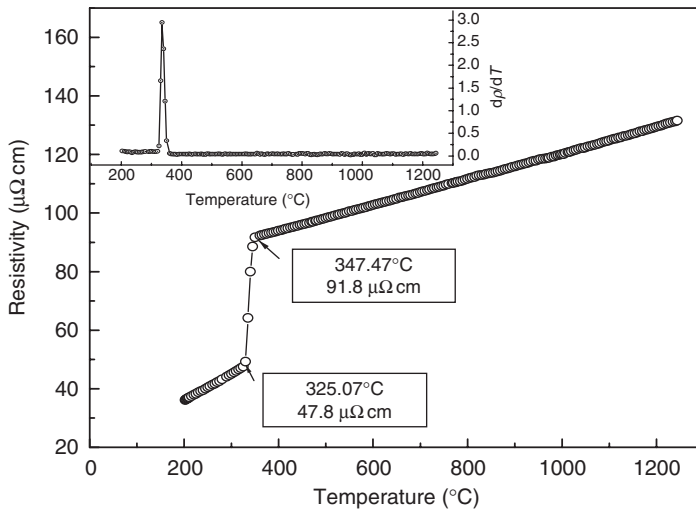


Figure 1. The resistivity–temperature curve of pure Pb. Inset shows $d\rho/dT$ vs. temperature.

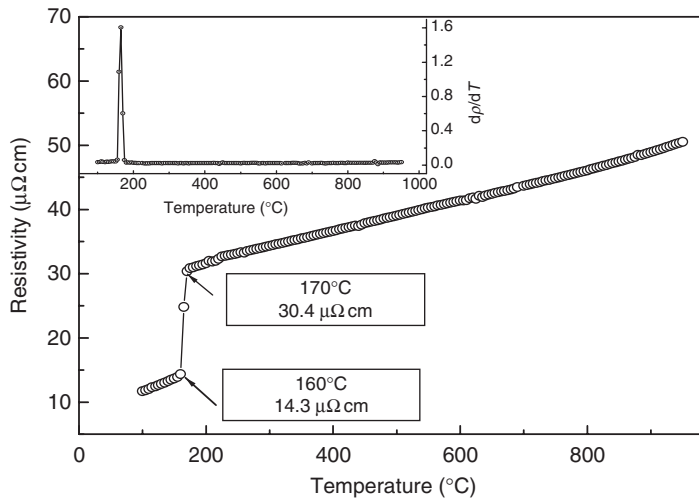


Figure 2. The resistivity–temperature curve of pure In. Inset shows $d\rho/dT$ vs. temperature.

from 47.8 to 91.8 $\mu\Omega\text{ cm}$ and from 14.3 to 30.4 $\mu\Omega\text{ cm}$ respectively, which is attributed to the fact that liquid metals with a relatively disordered arrangement of ions have higher resistivities than crystalline solid metals with more regular arrangement. The electrons mean free path is shorter when the electrons are moving through the disordered liquids, so the increase in electrical resistivity is to be expected [25]. After completely melting, their resistivities are all linear with increasing temperature over the whole experimental range, showing that no L–L structural transition takes place in pure Pb and In melts.

Figure 3 shows ρ – T curves of five Pb–In melts with different compositions, which are totally different from that of pure Pb and In melts. It can be found that the ρ – T curves of the Pb–In alloys are no more linear with increasing temperature after melting. In addition, we can clearly sign the turning points of each Pb–In alloy from the curve of ρ – T coefficients ($d\rho/dT$), which is inserted as an inset on the top left corner of each ρ – T curve. Starting transition temperature (T_S) and ending transition temperature (T_E) are marked in each ρ – T curve. Before T_S , the value of $d\rho/dT$ remains almost steady. But after T_S , the $d\rho/dT$ changes with increasing temperature. After T_E , the $d\rho/dT$ becomes stable again. Table 1 reports the temperatures of T_S and T_E and other related data.

All the above experimental results indicate that some L–L structural changes have taken place at the temperature range between T_S and T_E in the corresponding alloy melts, since resistivity is a sensitive parameter to the structure. In order to confirm the results of the resistivity method, we carried out the DSC experiment on the Pb–63%In melts (NETZSCH DSC 404, heating rate $20^\circ\text{C min}^{-1}$) chosen from all the compositions for its special (α) structure in solid state. Figure 4 is the result of DSC on a Pb–63%In sample, which shows that the thermal absorption peak position corresponds roughly to that of the relevant abnormal transition zone of electrical resistivity far above T_L but with a lagging to some extent due to a higher heating rate. The calorific effect in the DSC curves means that the system entropy of Pb–In melts undergoes a discontinuous change during the L–L transition, which also proves that it is feasible to explore the L–L structure transition by the resistivity method.

According to the nearly free electron (NFE) model [26], the electrical conductivity of liquid alloys is given by

$$\sigma = \frac{n_e e^2 L_0}{\hbar k_f} = \frac{1}{\rho} \quad (1)$$

where n_e and e are the electron density and charge, respectively. k_f , L_0 and \hbar are the Fermi wave number, mean free path of conduction electrons and Planck constant, respectively.

Based on the NFE model, it can be theoretically assumed that the abnormal changes on ρ – T curves can be attributed to the change in n_e due to the breaking of previous atomic bonds, or the change in mean free path L_0 of conduction electrons. It is generally accepted that the atomic bonds of crystals are only partly broken on melting, and the SROs derived from the corresponding solid crystal remain still in liquids even at a high temperature range. Therefore, it can be found that the resistivity of Pb–In melts changes continuously and almost linearly with increasing temperature before T_S (figure 3). As to the unusual varieties of ρ , we can put forward the following assumption: When the melts are heated to T_S , the kinetic energy of the atoms becomes high enough to overcome the energy barrier. Thus the previous meta-stable atomic

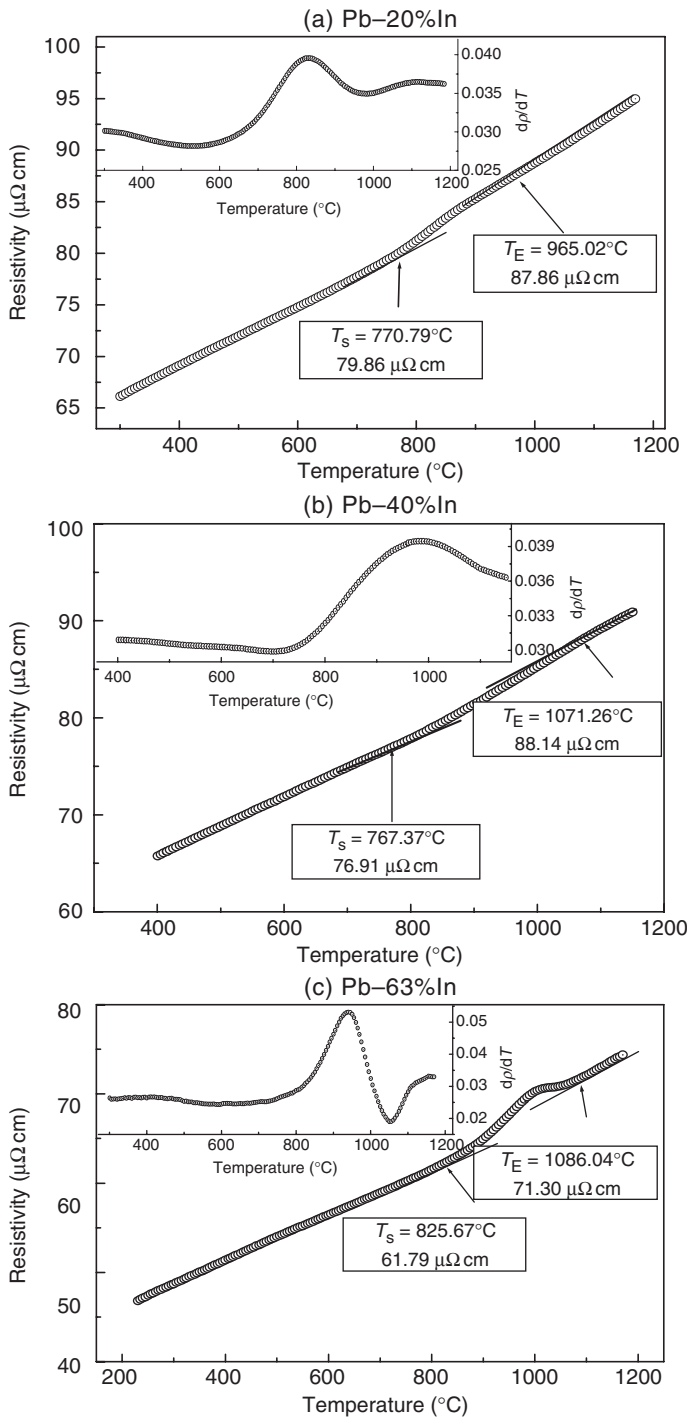


Figure 3. The resistivity–temperature curves of Pb–In alloys, for various compositions. Solid lines are linear fits to the $T < T_s$ and $T > T_E$ regimes, respectively. Insets show $d\rho/dT$ vs. temperature.

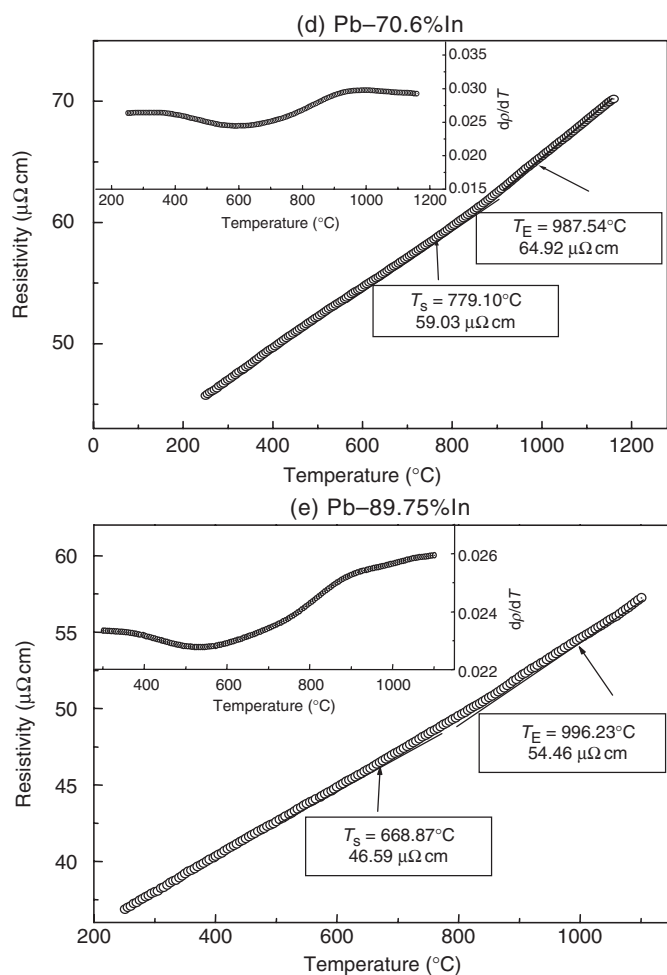


Figure 3. Continued.

Table 1. The comparison of ρ - T curves of Pb-In melts.

Ingredient	T_S (°C)	ρ at T_S ($\mu\Omega$ cm)	$d\rho/dT$ (before T_S) ($\mu\Omega$ cm K^{-1})	T_E (°C)	$d\rho/dT$ (after T_E) ($\mu\Omega$ cm K^{-1})
Pb-In (20 wt%)	771	79.86	0.0289	965	0.03625
Pb-In (40 wt%)	767	76.91	0.0303	1071	0.03623
Pb-In (63 wt%)	826	61.79	0.0255	1086	0.03246
Pb-In (70.6 wt%)	779	58.72	0.0252	988	0.02971
Pb-In (89.75 wt%)	669	46.59	0.0228	996	0.0259

T_S , starting transition temperature; T_E , ending transition temperature.

bonds begin to disappear gradually or the previous atomic clusters begin to become smaller, which make the high temperature liquid more disordered. Such a structural transitions of the liquid include the altering of bonds style, the nearest neighbour distance and the first coordination number, etc. All these changes will affect n_e and L_0 ,

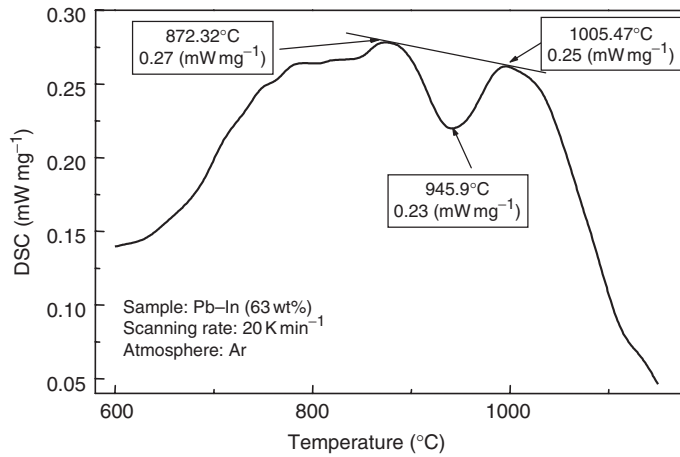


Figure 4. Result of DSC on the melt Pb–63%In.

which in turn will lead to the observed unusual change of ρ . Above T_E , the previously mentioned structural changes are completed, so the liquid exhibits stabilization and homogeneity at the microscopic scale. Therefore it is found that the resistivity increases linearly with increasing temperature again after T_E .

At the same time, we could see that the transition temperatures are different in Pb–In melts with various compositions, which indicates that the residual atomic clusters with crystal structures play an important role. When melts are heated at a sufficiently high temperature, atomic bonds are broken. According to Darken atomic diffusion theory, the diffusion coefficient can be described by:

$$D_{\alpha\beta} = (X_\beta D_\alpha + X_\alpha D_\beta)(1 + \ln f_\alpha / d \ln X_\alpha) \quad (2)$$

where f_α is the activity coefficient of component α , and D_α and D_β are the self-diffusion coefficients of components α and β , respectively. From equation (2), it follows that the diffusion coefficient changes with the composition of the alloy. Moreover, based on Eyring thermo-activation energy theory, diffusion coefficient *versus* temperature and activation energy is expressed by:

$$D = D_0 \exp(-\Delta Q/RT) \quad (3)$$

where ΔQ is the activation energy, R is gas constant and T is temperature. From equations. (2) and (3), it is evident that the activation energy required by the atomic migration is different for various compositions, so transition temperatures and degrees are different for different alloying composition. From table 1, it can be seen that T_S of Pb–63%In and Pb–70.6%In melts are higher than those of other compositions. It is assumed that the alloys with β in solid state are more stable than other compositions when they are heated above liquidus.

4. Conclusions

In comparison with the resistivity of pure liquid Pb and In, an unusual behaviour of the resistivity was found in the five compositions of Pb–In alloy studied in this article.

It can be concluded that the unusual behaviour of resistivity is caused by the occurrence of structural changes in the melts. Furthermore the thermal absorption peak in DSC curve of Pb–63%In melts confirms such a structural change. Such structural changes can be described as due to the fact that pre-formed atomic bonds are broken or pre-formed atomic clusters become smaller, thus making the high temperature liquid more disordered. The structural transition temperatures are different with various compositions and the intermediate phase (α) Pb–63%In and Pb–70.6%In alloys have higher transition temperatures than other compositions.

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