

Abnormal resistivity and viscosity behavior in Sb-rich Pb–Sb melts

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Abstract: Electrical resistivity and viscosity of Pb–Sb alloys are measured to investigate Peierls distortion behavior in the melts. In $\text{Pb}_{30}\text{Sb}_{70}$, $\text{Pb}_{20}\text{Sb}_{80}$, and $\text{Pb}_{10}\text{Sb}_{90}$ melts, temperature dependence of resistivity deviates from linear dependence during cooling. At 663 °C, different trends in isothermal behavior between experimental and theoretical resistivities, are interpreted as the existence of Peierls distortion in Sb-rich melts. In $\text{Pb}_{30}\text{Sb}_{70}$ and $\text{Pb}_{20}\text{Sb}_{80}$ melts, abnormal viscosity results verify the existence of abnormal structure transition, which is attributed to the formation of large Sb clusters with Peierls distortion. In undercooled liquid $\text{Pb}_{20}\text{Sb}_{80}$, minute resistivity coefficient and quadratic resistivity behavior are interpreted as the rapid increase of cluster size of Sb clusters with Peierls distortion, which provides preferential nucleation sites for higher structure similarity to the crystalline and lower liquid–solid interfacial energy.

Key words: electrical resistivity; viscosity; Peierls distortion; undercooled liquid; Pb–Sb alloys

1 Introduction

In crystalline group V elements with valence-electronic configuration s^2p^3 , the s level lies far below (≈ 8.4 eV) p level, and generally does not participate in the bonding. Thus, the bonding is dominated by half-filled p orbitals, in which the directions of neighbor lobes are orthogonal. Therefore, the most possible crystal structure should be a simple cubic [SC] structure. However, such a structure is unstable in electronic structure. To stabilize the crystal, six nearest neighbors of the SC structure split into three first nearest neighbors and three next nearest neighbors. Then, the SC structure has a Peierls distortion, which results in A7 structure. Recently, a reversible phase transition of crystal structure coupled with a semiconductor \rightleftharpoons metal transition was observed in GeTe alloys under pressure [1]. It was believed to be mediated by Peierls distortion. It was reported that Peierls distortion was crucial in metallic–insulator transition [2] and ferromagnetic properties [3]. Peierls distortion also played an important role in screw dislocation mobility [4] and lattice transition [5], which indicated its significance in nucleation and crystal growth. Then, probe into Peierls distortion deeply is of importance both in scientific and technological

perspective.

The existence of Peierls distortion is established in crystalline phase of group V elements. And it has drawn many scientific interests that the Peierls distortion survives in the melts [6]. The existence of Peierls distortion was verified by the neutron diffraction [7] and linear muffin tin orbital simulations study [8] on liquid As, which indicated that the distortion was independent of crystalline periodicity. The distortion was also demonstrated to exist in liquid As-based alloys for high distortion energy and thermal stability [9,10]. But for liquid pure Sb, it has been controversial about whether the Peierls distortion survives or not. This situation may be due to inconsistent structure researches on liquid Sb with different radiation methods [11–13]. However, as an effective indicator for structure transition [14–16], the electrical resistivity measurement was proved to be sensitive to the existence of Peierls distortion in liquid alloys which was often associated with the nonlinearity of the resistivity. In the heating process of liquid Sb, the nonlinear resistivity dependence on temperature was found by WANG et al [17]. It was interpreted as the surviving of Sb clusters with Peierls distortion, which were believed to be destroyed completely at higher temperature. In liquid Ga–Sb alloys, the nonlinear resistivity behavior with temperature was obtained in the

Ga₅₀Sb₅₀ and Ga₁₀Sb₉₀ (mole fraction) [17]. And in liquid In–Sb alloys, the nonlinear dependence of resistivity on temperature exhibited in the Sb concentration range of 50%–100% (mole fraction) [18]. The nonlinear resistivity behavior indicated that Sb clusters with Peierls distortion retained in these melts. However, the nonlinear resistivity behavior also exhibited in liquid Ga₅₀Sb₅₀ and In₅₀Sb₅₀, where the semiconductor compounds existed. Therefore, the identification of Peierls distortion would be disturbed by the semiconductor compound [19] retained in the group III–V melts. The neutron scattering studies on liquid As–Sb alloy indicated that, with Sb concentration higher than 85%, the melts retained all the structure features analogous to those of liquid Sb [9]. But in the liquid As–Sb alloys, the Peierls distortion in Sb clusters may be induced by As clusters, since the higher distortion energy in liquid As had been well established [7]. Therefore, the existence of Peierls distortion and its concentration range in liquid Sb–based alloys may be obscured due to the interaction between heterogeneous atoms in III–V and V–V alloys.

To avoid the possible disturbance in liquid III–V alloys and V–V alloys, simple eutectic Pb–Sb system was selected. In Sb-rich Pb–Sb melts, resistivity and viscosity measurement were performed to probe into melts structure evolution and Peierls distortion behavior.

2 Theory

The resistivity of liquid pure metals [20] can be obtained by

$$\rho = \frac{4\pi^3 \hbar Z^*}{e^2 k_F} \int_0^1 V^2(y) S(y) y^3 dy \quad (1)$$

where Z^* is the effective valence; k_F is the Fermi wave number; S is the structure factor; y is the wave number normalized by $2k_F$; V is the electron–ion pseudopotential form factor, following the description of ASHCROFT [21], which can be written as

$$V(y) = -\lambda^2 \cos(2yk_F R_{\text{core}}) / [y^2 + \lambda^2 f(y)] \quad (2)$$

where $\lambda = (\pi a_0 k_F)^{-1/2}$; a_0 is the Bohr radius; R_{core} is the effective core radius; $f(y)$ is the Lindhard scattering function.

According to extended Ziman theory, resistivity for liquid binary alloy [22] can be written as

$$\rho = \frac{4\pi^3 \hbar Z^*}{e^2 k_F} \int_0^1 \{xV_2^2(y)S_{22}(y) + 2[x(1-x)]^{1/2} \cdot V_2(y)V_1(y)S_{12}(y) + (1-x)V_1^2(y)S_{11}(y)\} y^3 dy \quad (3)$$

where x is the concentration of element with a large atomic radius; Z^* is the effective valence; S_{11} , S_{12} , S_{22} are

partial structure factors; V_1 and V_2 are pseudopotential form factors for the two elements, respectively.

Viscosity of liquid metals and alloys is a function of temperature. A well-known formula describing the temperature dependence of viscosity of liquids is the Arrhenius equation:

$$\eta = A \exp[E_v / R(t + 273)] \quad (4)$$

in which A is a pre-exponential factor; E_v is the energy of activation for viscous flow; t is the Celsius temperature.

3 Contactless device

In a uniform periodic external magnetic field H with angular frequency ω , for a cylinder non-ferromagnetic sample with isotropic resistivity ρ , the alternating field H_s inside the sample can be obtained by Maxwell's equations following electromagnetic induction. Based on effective permeability μ_{eff} , H_s can be expressed as $H_s = \mu_{\text{eff}} H$. According to Faraday's law and Kirchhoff's second law, differential voltage between effective voltages induced in the signal receiving coils and the reference coils can be described as

$$\Delta U = K \left[\left(\left| \mu_{\text{eff}} \right| - \frac{\mu_{r0}}{\mu_r} \right) / \left(\left| \mu_{\text{eff}} \right| - \frac{\mu_{r0}}{\mu_r} + \frac{2lS}{l_s S_s} \times \frac{\mu_{r0}}{\mu_r} \right) \right] \quad (5)$$

where l_s and S_s are the length and cross-sectional area of the sample, respectively; l and S are the length and cross-sectional area of the coils; μ_{r0} and μ_r are the relative permeabilities of air and the sample respectively; K is a constant dependent on the circuit and working frequency. When the working frequency is fixed during the measurement, the resistivity can be obtained by the received voltage. The fluctuation in contactless resistivity was about 3%. Further details of the contactless measurement device could be found in Refs. [23,24].

4 Experimental

Pb and Sb used in the experiments had the purities of 99.99%. The alloys were pre-melted in furnace under 99.999% argon gas. The error in composition did not exceed 0.5% with the consideration of mass loss. During the resistivity measurements in four-electrode method, 99.999% pure argon gas was used to protect the alloys from oxidation. The temperature was obtained by a calibrated S-type thermocouple. The accuracy of the temperature measurement was ± 1 °C. To eliminate the error due to temperature fluctuation, each data point was obtained after the temperature was held for about 20 min before measurement. The accuracy of the resistivity

measurements was estimated to be 0.5%. For the contactless measurement, standard quartz tubes were used in the location of samples. The temperature was simultaneously detected with a pyrometer (Raytek 3i). With the help of glass fluxing technology [25,26], the melts were undercooled successfully since there was a recalescence about 25 °C in temperature—time curves.

Viscosity measurements were carried out by a torsional oscillation viscometer for high—temperature melts [27,28]. The samples were held in a sealed SiO₂ cylindrical crucible suspended on a Mo wire. The torsion oscillation was damped by the friction with the melt. Then, the dynamic viscosity of the liquid sample can be obtained [29].

5 Results and discussion

Figure 1 presents the temperature dependence of resistivity in liquid Pb and Pb–Sb alloys by four-electrode method during the cooling process. As it is shown, resistivity decreases linearly with decreasing temperature when Sb concentration ranges from 0 to 60%. While the resistivity data of liquid Pb₂₀Sb₈₀ and Pb₁₀Sb₉₀ can be fitted very well with the quadratic dependence of temperature. Temperature dependence of resistivity in Pb₃₀Sb₇₀ melts seems to be linear; however, it is not convincing at the low temperature owing to the large temperature interval between data points. Generally speaking, resistivity results from electron–ion interaction, and it decreases linearly with temperature in simple liquid metals and alloys [30] during the cooling process. Then, liquid Pb and Pb–Sb alloys with Sb concentration less than 60% are believed to be simple melts. And it is reasonable to conclude that abnormal structure transition exists in Pb₂₀Sb₈₀ and Pb₁₀Sb₉₀ melts. During the heating process, Sb clusters with Peierls distortion similar to solid phase were verified to exist in the melts in the vicinity of liquidus of pure Sb [17]. Then, resistivity deviates from linear dependence of temperature owing to the destruction of Peierls distortion in these Sb clusters and the releasing of free electrons bounded by the covalent bond [17]. Accordingly, it is meaningful to assume that Peierls distortion reforms in liquid Pb₂₀Sb₈₀ and Pb₁₀Sb₉₀ during the cooling process. Then during the cooling process, on one hand, the reformation of Peierls distortion with covalent bonds decreases the density of free electrons and increases electron scattering. On the other hand, for Pb atoms and Sb atoms that do not involve in Peierls distortion in the melts, the scattering effect on free electrons decreases due to density fluctuation with temperature. Due to the low content of Sb atoms with Peierls distortion surviving in the melts, the latter factor (temperature) takes the dominant role

and thus resistivity decreases with decreasing temperature. It should be mentioned that, more and more Sb atoms involve in Peierls distortion to stabilize the melts during cooling, which upward deflects the resistivity curves. As an overall effect of these two facts, the resistivity behavior is nonlinear in liquid Pb₂₀Sb₈₀ and Pb₁₀Sb₉₀.

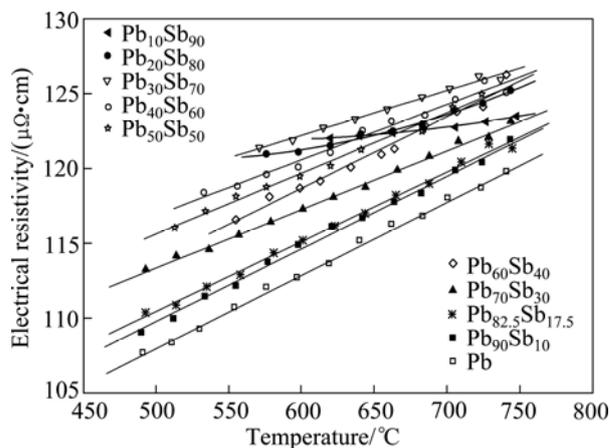


Fig. 1 Temperature dependence of resistivity in liquid Pb and Pb–Sb alloys using four-electrode method

For understanding temperature dependence of resistivity in liquid metals and alloys, Ziman theory provides theoretical basis. In the liquid Pb–Sb alloys, the locations of the main peak in structure factor are at 21.53 and 21.50 nm⁻¹, respectively, which are at the left side of 2k_F [11,31]. Then the resistivity behavior with temperature of Pb–Sb alloys can be interpreted as that of polyvalent metals [18]. As the temperature decreases, the intensity of main peak in structure factor increases and the width narrows. According to Eq. (1), the integral value is mainly dependent on the width narrowing rather than the intensity increasing. This results in that the resistivity of liquid Pb–Sb alloys decreases with decreasing temperature.

The isothermal resistivity dependence on concentration of liquid Pb–Sb alloys has been studied at 663 °C. As shown in Fig. 2, liquid Pb exhibits the minimum resistivity. The resistivity increases with increasing concentration of Sb, when Sb concentration is no more than 70%. This means that the addition of Sb atoms increases the scattering section area for electrons and thus the resistivity increases. But in the regions with Sb concentration no less than 70%, it is very interesting that the experimental resistivity decreases with decreasing Sb concentration. Volume dependent pseudopotential was widely used for understanding resistivity of liquid polyvalent alloys [32], where theoretical results were in good agreement with experimental results. Thus, the hard-sphere structure factor [33] and volume dependent pseudopotential are used in calculation of

resistivity at 663 °C. Following Eqs. (2) and (3), the calculated resistivity results for liquid Pb–Sb alloys are shown in Fig. 2.

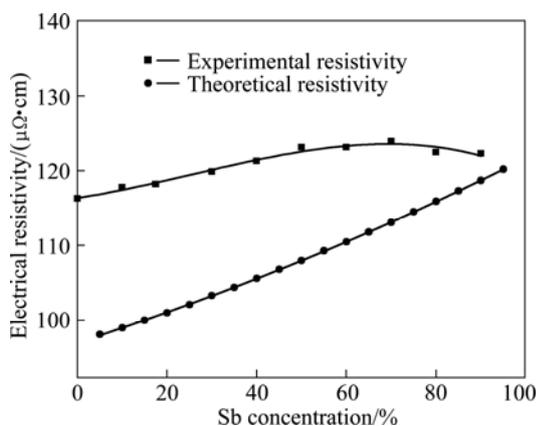


Fig. 2 Experimental and theoretical isothermal resistivity of liquid Pb–Sb alloys at 663 °C

As shown in Fig. 2, when Sb concentration is no more than 70%, both the experimental and theoretical results increase with increasing Sb concentration. Therefore, the volume-dependent pseudopotential and hard-sphere structure factors are effective to understand the resistivity behavior in liquid Pb–Sb alloys. But in the regions with Sb concentration higher than 70%, the decrease of experimental results with increasing Sb concentration can not be interpreted in Ziman theory. This may result from that abnormal structure existing in the melts can not be described by hard-sphere structure factors. Liquid Pb is generally believed to be simple metal in structure. Pb–Sb alloys are simple eutectic system, and no intermetallic compound has been reported in solid phase. All these facts indicate that the origin of abnormal structure is related to local structure between Sb atoms. Taking the existence of Peierls distortion in liquid Sb into consideration, it is deduced that Sb clusters with such distortion also exists in the Pb–Sb alloys when Sb concentration is higher than 70%. On the other hand, the existence of Peierls distortion means the high structure similarity to solid phase and high structure ordering. To a degree, the high structure ordering will decrease the electron scattering. This is consistent with experimental result of isothermal resistivity.

Viscosity is an important parameter sensitive to structure transition in metallic melts. Temperature dependence of viscosity in liquid Pb₄₀Sb₆₀, Pb₃₀Sb₇₀ and Pb₂₀Sb₈₀ melts is plotted in Fig. 3. Obviously, viscosity of liquid Pb₄₀Sb₆₀ can be well fitted in Arrhenius equation (Eq. (4)), reflecting the continuous transition in local structure. While there is an inflection in the viscosity curves of Pb₃₀Sb₇₀ and Pb₂₀Sb₈₀ melts, implying the existence of abnormal structure change.

Their inflection temperatures (T_i) are about 620 and 720 °C, respectively. These results are in good agreement with resistivity results. The high transition temperature implies the high stability of Peierls distortion in Pb₂₀Sb₈₀ melts. As shown in Table 1, it is noteworthy that, there is a significant increase in the activation energy of viscous flow when abnormal structure transition occurs. This indicates some large clusters form during the cooling process in the melts. In crystalline phase Sb, Peierls distortion occurs and charge–density–wave length–range order is nearly achieved [34]. And Peierls distortion was verified to be related to medium–range order in Sb melts [34]. Taking its existence in the melts into consideration, it is reasonable to conclude that the large clusters are in relation with Sb clusters with Peierls distortion.

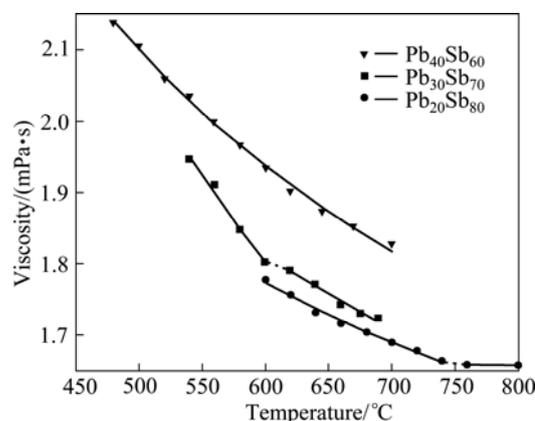


Fig. 3 Temperature dependence of viscosity in liquid Pb–Sb alloys (Thin solid lines denote the fitted Arrhenius plots. Dot line denotes the structure transition temperature range.)

Table 1 Parameters of viscosity fitted following Arrhenius equation

Alloy	$(E_v/R)/K$		$A/(mPa\cdot s)$	
	Above T_i	Below T_i	Above T_i	Below T_i
Pb ₄₀ Sb ₆₀	543.33		1.04	
Pb ₃₀ Sb ₇₀	442.40	458.08	1.13	1.10
Pb ₂₀ Sb ₈₀	64.81	410.30	1.56	1.11

Electrical resistivity of undercooled liquid Sb–rich alloys has never been reported, which is also of importance to understand the electron behavior and Peierls distortion behavior in metastable state. Therefore, it is necessary to measure the resistivity continuously in contactless method from superheated to undercooled liquid state, to get more information about the melts behavior. With the help of glass fluxing technology, a maximum undercooling of about 25 °C is obtained for liquid Pb₄₀Sb₆₀, Pb₃₀Sb₇₀ and Pb₂₀Sb₈₀. As shown in Fig. 4, the recalescence about 25 °C is visible on the temperature–time curves. And the resistivity is simultaneously measured in contactless method.

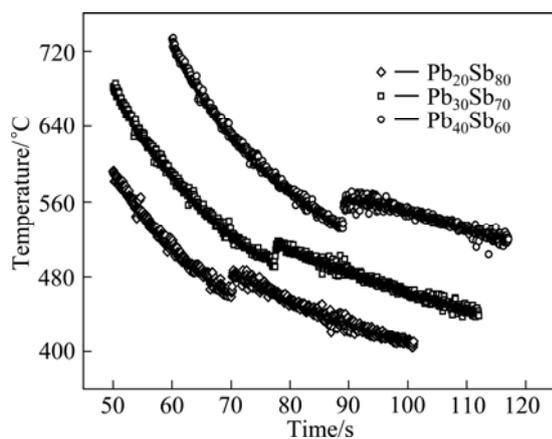


Fig. 4 Time curves of temperature during resistivity measurement in contactless method

As shown in Fig. 5, the contactless resistivity of $\text{Pb}_{40}\text{Sb}_{60}$, $\text{Pb}_{30}\text{Sb}_{70}$ and $\text{Pb}_{20}\text{Sb}_{80}$ melts is vertically shifted for clarity. Temperature dependence of resistivity is linear in liquid and undercooled liquid states, which indicates that Peierls distortion does not exist in $\text{Pb}_{40}\text{Sb}_{60}$ melt. But in the alloys with Sb concentration higher than 60%, the resistivity—temperature curves exhibit a deviation from linear dependence. For liquid $\text{Pb}_{30}\text{Sb}_{70}$, a clear turning of the temperature coefficient of resistivity (TCR) is found at about 620 °C. And constant temperature coefficients exhibit before and after the inflection, respectively. This is interpreted as that Peierls distortion reforms in liquid $\text{Pb}_{30}\text{Sb}_{70}$ during the cooling process, which does not conflict with four-electrode resistivity data shown in Fig. 1. The contactless resistivity of $\text{Pb}_{20}\text{Sb}_{80}$ exhibits a quadratic dependence on temperature above the liquidus and in undercooled state, when the temperature is below 735 °C. It is in good accordance with four-electrode data. What's more, these are in good agreement with viscosity results, taking the transition temperature into consideration. These results support the reformation of Peierls distortion during the cooling process. Compared to liquid $\text{Pb}_{30}\text{Sb}_{70}$, the inflection temperature in resistivity is higher (about 735 °C) in liquid $\text{Pb}_{20}\text{Sb}_{80}$. This means that the temperature at which the Peierls distortion reforms is lower in liquid $\text{Pb}_{30}\text{Sb}_{70}$, and it also implies that the thermal stability of Peierls distortion is lower in liquid $\text{Pb}_{30}\text{Sb}_{70}$. It can be attributed that the addition of Pb atoms decreases the thermal stability of Peierls distortion in liquid Pb–Sb alloys, since the interaction between Sb atoms would be weakened. The facts that Peierls distortion never reforms in $\text{Pb}_{40}\text{Sb}_{60}$ may be due to weak interaction between Sb atoms and low thermal stability of Peierls distortion in liquid and undercooled alloys.

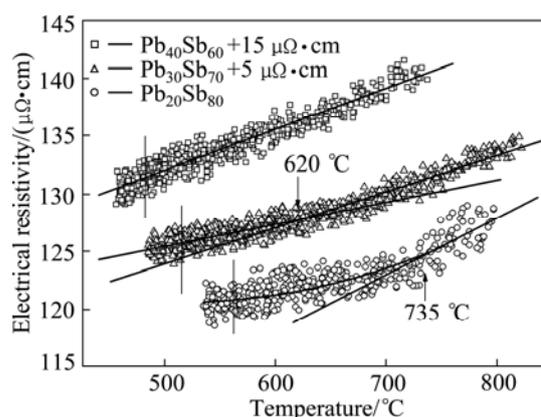


Fig. 5 Contactless resistivity of liquid and undercooled Pb–Sb alloys in Sb concentration range of 60% to 80% (The vertical thin lines denote liquidus of the alloys)

As shown in Fig. 5, no abnormal change is found in resistivity round the liquidus temperature. It implies that the melt structure continuously changes when it comes into undercooled liquid state. This indicates the existence of Peierls distortion in the undercooled $\text{Pb}_{30}\text{Sb}_{70}$ and $\text{Pb}_{20}\text{Sb}_{80}$ melts. Below 620 °C, linear resistivity—temperature behavior exhibits in $\text{Pb}_{30}\text{Sb}_{70}$, which is similar to other liquid Sb–based alloys in the concentrations with Peierls distortion [17,18]. While quadratic resistivity dependence and minute resistivity coefficient exhibit in undercooled $\text{Pb}_{20}\text{Sb}_{80}$, as shown in Fig. 5. The quadratic resistivity behavior implies abnormal structure evolution in undercooled $\text{Pb}_{20}\text{Sb}_{80}$ melt. In hypereutectic Pb–Sb alloys, Sb is primary phase in the solidification process and it provides nucleation sites. And as potential nuclei, the size of Sb clusters will increase with decreasing temperature. In the regions where Peierls distortion exists, the similarity of structure in the melts to that in the crystalline phase is higher due to the existence of Peierls distortion. The higher structural similarity would lead to lower solid–liquid interfacial energy and smaller activation threshold for Sb clusters with Peierls distortion during nucleation. Therefore, Sb clusters with Peierls distortion are regarded as preferential crystalline embryos. During the cooling process, the increase in activation energy of viscous flow indicates the rapid increase in cluster size, as shown in Fig. 3. As crystalline embryos, the increase of the size of Sb clusters with Peierls distortion does not stop until nucleation occurs. In $\text{Pb}_{20}\text{Sb}_{80}$ melt, larger Sb clusters size means that more Sb atoms involve in Peierls distortion and more free electrons are bounded by covalent bonds. Thus larger clusters size means that stronger scattering effect is exerted on electrons. These weaken the dominant role of temperature in resistivity behavior in undercooled state. And then, the minute TCR and quadratic resistivity behavior exhibit in undercooled

Pb₂₀Sb₈₀. Similarly, in previous studies of TIAN [35], the abnormal increase of cluster size was found in undercooled Cu₇₀Ni₃₀ alloy. And in the same concentration range of Cu–Ni alloys, the quadratic resistivity–temperature behavior was obtained [36], which indicated the existence of associations in the vicinity of liquidus. Analogously, quadratic resistivity behavior implies the increase of clusters size in liquid and undercooled liquid Pb₂₀Sb₈₀. Due to the high Pb concentration and low thermal stability of Peierls distortion in Pb₃₀Sb₇₀ melt, the increase of clusters size is restricted and linear resistivity behavior is obtained in undercooled liquid state.

Abnormal temperature dependence of resistivity and viscosity in Sb-rich Pb–Sb alloys indicates the existence of abnormal structure change during the cooling process. However, the resistivity does not come back to linear dependence just before the abrupt change. This is a little different from the liquid–liquid structure transition (LLST) induced by temperature [37–39]. And the increase of clusters size with decreasing temperature is irreversible in the present results. To promote preparing materials with high performance [40] and reveal the relationship between LLST and Peierls distortion in Pb–Sb alloys, much work concentrated on the structure research should be performed in further study.

6 Conclusions

1) In the regions with Sb concentration no less than 70%, the inflection in temperature dependence of resistivity is interpreted as the reformation of Peierls distortion during the cooling process. Around the same temperature, the increase in activation energy of viscous flow verifies the formation of large clusters. These verify the existence of abnormal structure change during the cooling process, which is well interpreted as the reformation of Sb clusters with Peierls distortion.

2) Temperature dependence of resistivity continuously changes when the melts come into undercooled liquid state. The existence of Sb clusters with Peierls distortion in undercooled state is verified by resistivity behavior. In undercooled liquid Pb₂₀Sb₈₀, the quadratic resistivity behavior and minute TCR are interpreted as the rapid increase of the size of Sb clusters with Peierls distortion.

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富锑铅锑熔体电阻率及黏度的异常变化

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摘 要: 通过测量 Pb–Sb 合金熔体的电阻率及黏度, 探讨熔体中 Peierls 畸变的演变。Pb₃₀Sb₇₀、Pb₂₀Sb₈₀ 和 Pb₁₀Sb₉₀ 在降温过程中具有非线性电阻率温度关系。在 663 °C 下, 实验与计算的等温电阻率成分关系的变化趋势不同, 也暗示了富 Sb 熔体中 Peierls 畸变的存在。Pb₂₀Sb₈₀ 与 Pb₃₀Sb₇₀ 熔体的异常的黏度–温度关系证实了异常结构转变的存在, 这种异常转变被认为是具有 Peierls 畸变的大尺寸 Sb 团簇的形成。在过冷液态 Pb₂₀Sb₈₀ 中, 由于提高了熔体与晶态固体的结构相似性并降低了液固界面能, 含有 Peierls 变的 Sb 团簇在凝固过程中提供优先的形核位; 抛物线的电阻率–温度关系及极小的电阻率系数被认为是由这些 Sb 团簇尺寸的快速增加而导致的。

关键词: 电阻率; 黏度; 皮尔斯畸变; 过冷液态; 铅锑合金

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