Kinetics of the liquid-liquid transition of Pb-Sn melts

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Abstract

Through isothermal experiments, we investigated the time evolution of electrical resistivity of temperature induced liquid-liquid structure transition (LLST) in PbSn liquid alloys with different compositions: hypoeutectic PbSn40wt.%, hypereutectic PbSn80wt.% and eutectic PbSn61.9wt.%. We found that the kinetic transition process is nucleation-growth type, and has different transition models with the change of composition: the Johnson-Mehl-Avrami model at the eutectic point and the autocatalytic reaction model at the hypoeutectic and hypereutectic composition region. The mechanisms of the autocatalysis and the transition kinetics have been roughly discussed. The result of research could be beneficial for further understanding of the essence of LLST.

Key words: liquid structure transition; electrical resistivity; activation energy

1. Introduction

Liquid-liquid transition is the transformation of a single-component liquid from one liquid state to another, the existence of which presents a challenge to our conventional sense that liquid is a unique state of matter. Many previous theoretical and experimental studies have provided indirect evidence for such transition in several materials: atomic liquids such as C, P, Si, Ge, Se, Rb, and Cs [1–8], network-forming liquids such as water, SiO_2 and GeO_2 [9–12], and ordinary molecular liquids. Recently, the results of our studies implied that an anomalous temperature induced LLST might occur far above the liquidus at ambient pressure in some binary alloys, e.g., In-Sn, Pb-Sn, Pb-Bi and In-Bi [13–15]. Tanaka even proposed that a LLST could, in principle, exist in any liquids covering atomic to molecular liquids [16].

Up to now, for molecular liquids, there are detailed studies on the kinetics of LLST [17–20]. For example, Kurita studied the time evolution of the heat flux during the liquid-liquid transition in triphenyl phosphate, and found different transition mode: nucleation-growth and spinodal-decomposition type [19]. However, for atomic systems, researches on the kinetics of the LLST are just at the beginning. For the temperature induced LLST of alloy melts, researches have been mainly focused on finding the pertinent transition phenomena in liquid metals or alloy systems, and on the kinetic behaviour there have been only few studies. In this paper we studied the kinetics during the LLST in PbSn melts, which is a convenient system to study LLST.

Through isothermal experiments we found that the kinetic transition process is nucleation-growth type in PbSn melts with various compositions [21, 22]. The time evolution of electrical resistivity could be described by different transition models with the change of composition: the Johnson-Mehl-Avrami model at the eutectic point and the autocatalytic reaction model when alloy composition departs from the eutectic point. The mechanism of autocatalysis on the transition process has been also discussed roughly from diffusion viewpoint.

2. Experiments

As a structure sensitive physical quantity, electric resistivity (ρ) is sensitive to the liquid structural change. According to the nearly free electron (NFE) model [23], the electrical conductivity of liquid alloys is given by $\rho = hk_\mathrm{f}/n_\mathrm{e}e^2L_0$, where h and k_f are the Planck constant and the Fermi wave number, respec-

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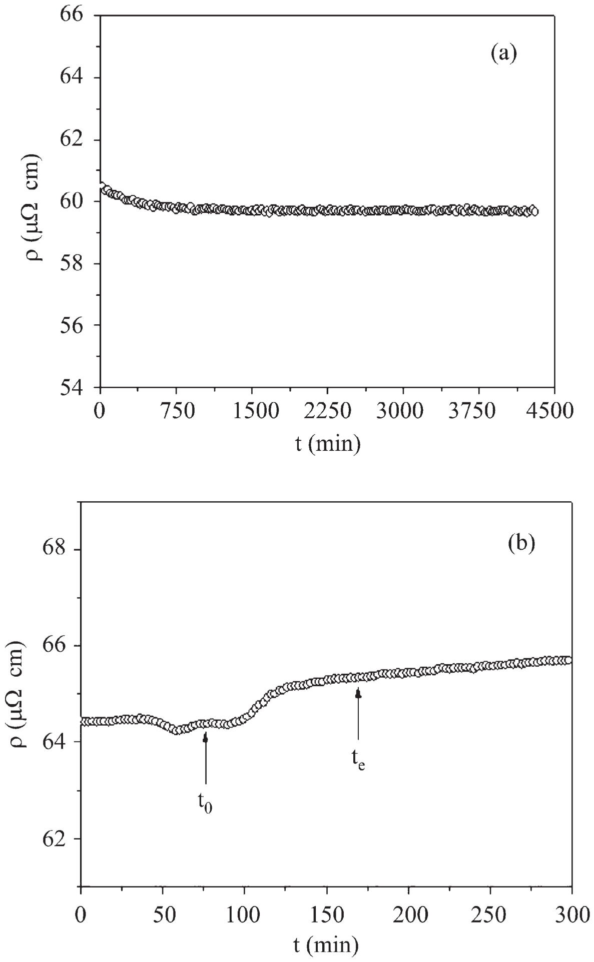


Fig. 1. Isothermal experiments held at different temperatures in Pb-Sn61.9 melt: (a) 500 ℃, (b) 615 ℃.

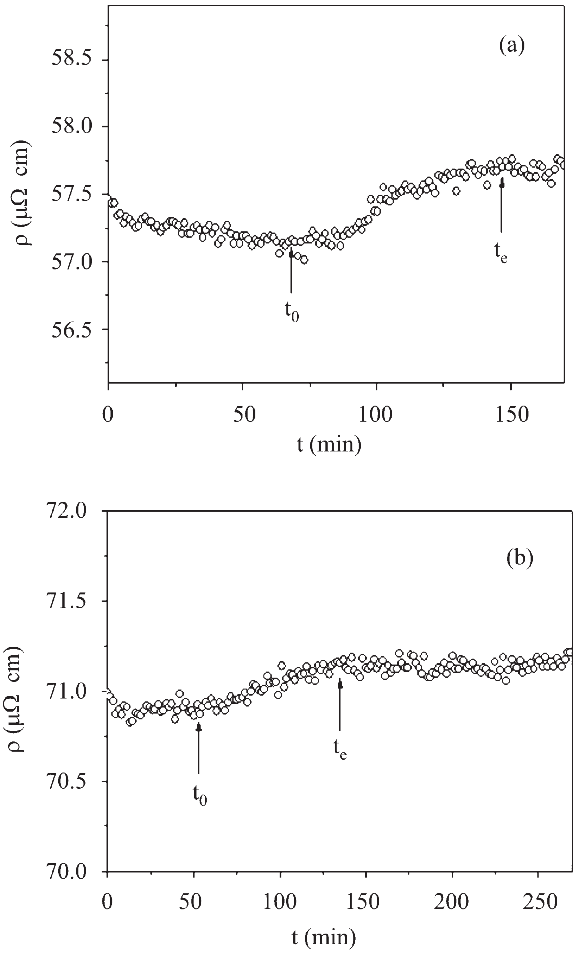


Fig. 2. Isothermal experiments held at 615 ℃ in PbSn80 and PbSn40 melts: (a) PbSn80, (b) PbSn40.

tively, n_e and L_0 are electron density and mean free path of conduction electrons, respectively. During the transition process, the change of L_0, which is induced by the change of short-range orders, will lead to obvious change of resistivity.

In this paper, the electrical resisitivity of Pb-Sn alloy melts has been measured by DC four-probe method. Weighted amounts of 99.99 % pure Sn and Pb were melted at 400 ℃ for over 30 minutes, then poured into measuring cells, and cooled to room temperature for the following experiment. The measuring cells 3.38 mm in diameter were made from silica glass. The thermal expansion of the silica glass was so small that the variation of 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 by KEITHLEY-2182 nanovoltmeter, while constant current of 500 mA was supplied by the PF66M sourcemeter. The experimental details and equipment have been described elsewhere [24]. The resistivity measurements were carried out in purified argon media to protect the sample from oxidation.

3. Results and discussion

During isothermal experiments, samples are heated rapidly (about 300 K min^{-1}) and then held at the appointed temperatures: 500 ℃ and 615 ℃ for PbSn61.9 melt, 615 ℃ for PbSn80 and PbSn40 melts. The curves of resistivity versus time (ρ-t) are shown in Figs. 1 and 2.

Held at different temperatures, the resistivity of PbSn61.9 reveals different kinetics phenomena. PbSn61.9 melt was held at 500 ℃ for 72 hours (Fig. 1a), and its resistivity is almost unchanged. It indicates that the liquid structure is steady at low temperatures and the influencing factors such as composition segregation could be neglected. However, after holding at 615 ℃ for 75 minutes, an S-shaped change occurs in ρ-t curve of PbSn61.9 (Fig. 1b), and the same

Table 1. The transition data of LLST of PbSn melts with different compositions

Different compositions (wt.%)	Transition beginning time t_0 (min)	Transition ending time t_e (min)	Total transition time $(t_e - t_0)$ (min)	ln K_T	d	Transition model
PbSn61.9	75	172	97	−15.38	–	J-M-A transition model
PbSn80	67	148	81	−2.22	0.028	autocatalytic reaction model
PbSn40	54	132	78	−2.68	0.075	autocatalytic reaction model

phenomenon is also observed in PbSn80 and PbSn40 melts (Fig. 2). Through tangent method, we selected t_0, t_e as the transition beginning time and ending time, respectively. The transition data have been listed in Table 1. It could be seen that for PbSn61.9 melt, its t_0, t_e and the total transition time $(t_e - t_0)$ are both longer than those of PbSn80 and PbSn40 melts, which reveals that the transition speed at eutectic point is slower than that of other compositions.

It is generally accepted that the atomic bonds of crystals are only partly broken at melting stage and the atomic clusters with the crystal structure are still remaining in liquids. In spite of long-range disorders and the energetic undulation, liquid structure is mainly composed of atomic clusters and a few free atoms less than 10 % locally [25, 26]. For Pb-Sn binary alloy melts, at the temperature not too far above the liquidus, liquid structure is metastable medium-range local ordering (liquid phase L_1) with lots of minor residual orders rich in either Pb or Sn. It has been verified by Dahlborg's work [27]. Obviously, from 500 ℃ to 615 ℃, it could be seen that liquid phase L_1 is steady at low temperatures, and with increasing temperature, liquid structure will gain enough energy to overcome the energy barrier ΔE (which is mainly composed of atomic bonding forces), and the Pb-Pb or Sn-Sn atomic bonds in phase L_1 are broken continuously. At the same time, the new Pb-Sn atomic bonds build up, by which the relatively uniform melt (liquid phase L_2) nucleates and grows, and gradually substitutes old liquid structure. The melt becomes a true solution, a completely mixed liquid state. That is, the phase transition L_1(Pb-Pb + Sn-Sn) $\rightarrow$ L_2(Pb-Sn) [14] takes place, which is an order-disorder liquid-liquid phase transition.

From the above analysis it could be seen that similar to normal solid-state phase transition, LLST process is also a kinetic process with new phase forming and old phase disappearing. From t_0 to t_e, the time evolution of structure transition fraction (x) could be deduced by the equation $x = (\rho_t - \rho_0)/(\rho_e - \rho_0)$, where ρ_0 is the resistivity at the time t_0, ρ_e is the resistivity at the time t_e, and ρ_t is the resistivity at time t. According to the analysis to the $x \sim t$ curves, it is found that the Pb-Sn LLST process has different transition model with the change of composition.

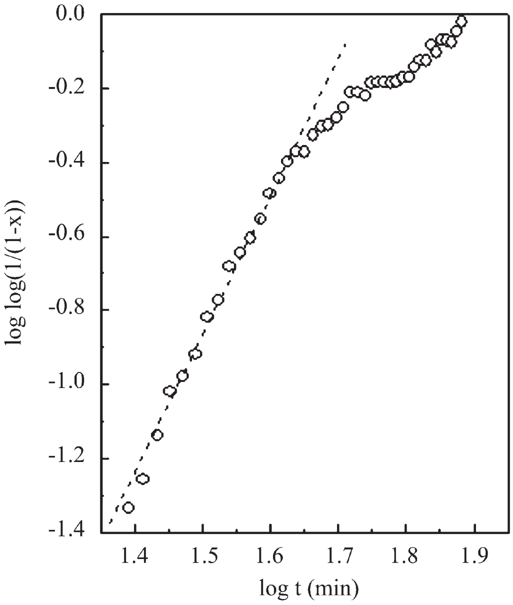
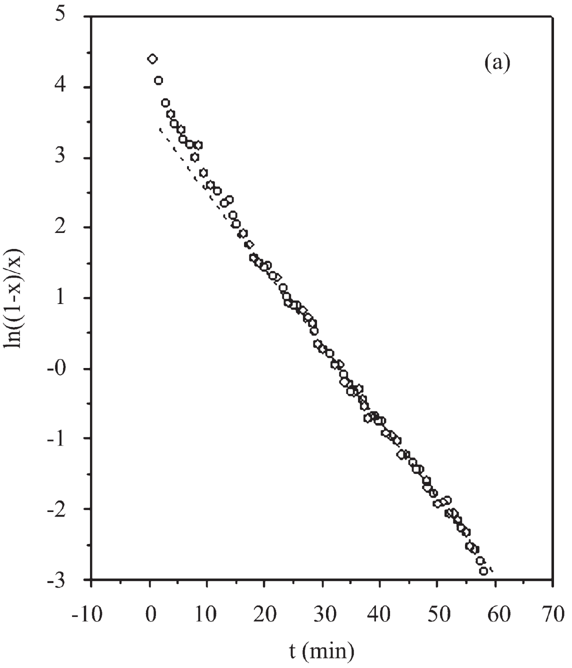


Fig. 3. Curve of $\log\log\left(\frac{1}{1-x}\right)$ versus $\log t$ in Pb-Sn61.9 held at 615 ℃ experiment.

For PbSn eutectic melt, the transition kinetic process fits J-M-A transition model well, which could be described as follows:

$$\log\log\frac{1}{1-x} = \log K_T + n\log t, \qquad (1)$$

where K_T is the reaction rate constant and n is Avrami exponent. With $\log\log 1/(1-x)$ and $\log t$ as variants, the curve is plotted in Fig. 3 ($x = 0.1 \sim 0.9$). It maintains approximately linear when $x < 0.8$, and then deviates from the linear line greatly. $\log K_T$ is calculated as −15.38, the value of which reflects transition speed and is much smaller than that of normal solid-state phase transition. Linear slope n is 3.87, which is an important parameter reflecting different transition pattern. It indicates that PbSn61.9 LLST process is of nucleation-growth type, and similar to solid



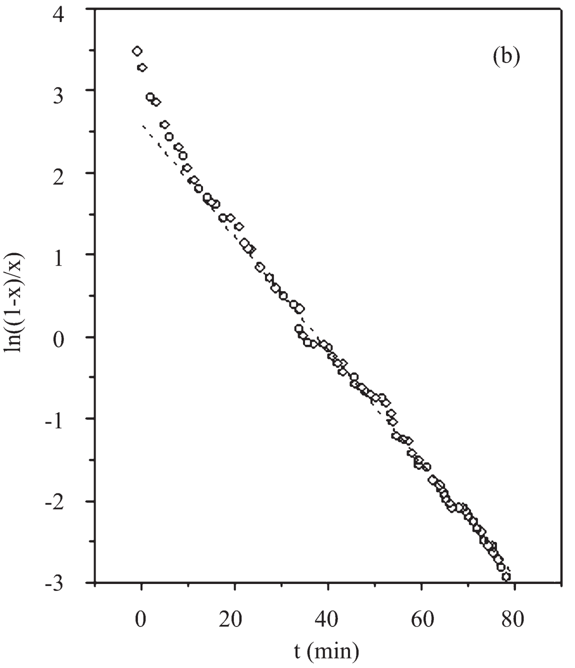


Fig. 4. Curve of $\ln\left(\frac{1-x}{x}\right)$ versus time in PbSn80 and PbSn40 held at 615 °C: (a) PbSn80, (b) PbSn40.

polymorphic transition process. Liquid phase II is nucleated randomly and homogeneously with nucleation rate decreased with time, and grows with a constant growth rate.

For PbSn40 and PbSn80 melts, different with J-M-A transition model of PbSn61.9 LLST, we found that their kinetic transition process could be described by the autocatalytic reaction model well, the equation is as follows:

$$\ln\left(\frac{1-x}{x}\right) + \ln d = -K_{\mathrm{T}}t, \tag{2}$$

where d is the initial catalyst concentration. The autocatalytic reaction model is also nucleation-growth type and the new generated phase has catalysis to the transition process. With $\ln{(1-x)/x}$ and t as variants, the curve is plotted in Fig. 4, and maintains approximately linear when $\ln{(1-x)/x} < 2$. For PbSn80 and PbSn40, $\ln K_{\mathrm{T}}$ are calculated as −2.22 and −2.68, respectively, and d are calculated as 0.028 and 0.075, respectively. Compared with PbSn61.9 LLST, $\ln K_{\mathrm{T}}$ of the two liquid alloys are both larger, and the transition speed of the two liquid alloys is faster correspondingly for catalysis.

According to the above analysis, LLST process of Pb-Sn melts could be simply described as $\mathrm{L_1}$(Pb-Pb + Sn-Sn) → $\mathrm{L_2}$(Pb-Sn), which is also an atomic rearrangement and diffusion process. We believe that there are superfluous atom clusters (rich in Pb or Sn) that do not take part in the transition process when the alloy composition leans to one component, and those superfluous clusters are distributed in the melt homogeneously. Based on Daken's [28] atomic diffusion theory, the diffusion coefficient could be described by:

$$D_{\alpha\beta} = (X_\beta D_\alpha + X_\alpha D_\beta)(1 + d\ln f_\alpha / \ln X_\alpha), \tag{3}$$

where f_α is the activity coefficient of component α, D_α and D_β are self-diffusion coefficients of components α and β, respectively. From this formula, we can see that the diffusion coefficient changes with the composition of components. Moreover, based on Eyring thermoactivation energy theory, the diffusion coefficient versus temperature and activation energy is expressed by:

$$D = D_0 \exp(-\Delta Q/RT), \tag{4}$$

where ΔQ is the activation energy, R is the gas constant and T is temperature. From these two formulae it is obvious that the activation energy required in atomic migration is different for different compositions.

What is the mechanism of autocatalysis during the liquid structure transition process? Obviously, as the transition progresses, the existence of those superfluous clusters will lead to increasing proportion difference between Pb-Pb clusters and Sn-Sn clusters, and the proportion change will be reflected in the melt local structure rapidly for the fluidity and diffusibility of liquid. It will reduce the value of ΔQ and accelerate the transition speed. So with the indirect catalysis of superfluous clusters, the whole LLST process of PbSn80 and PbSn40 melts reveals autocatalytic reaction model. For PbSn61.9 melt, we believe that the eutectic point is special to other compositions: atomic clusters fully take part in the transition process, and there are no superfluous clusters during the transition process.

4. Conclusion

In summary, by means of electrical resistivity, we investigated the kinetic behaviour of temperature-induced LLST process in PbSn alloys with different compositions: hypoeutectic PbSn40wt.%, hypereutectic PbSn80wt.% and eutectic PbSn61.9wt.%. Two different kinds of transition models have been found: the Johnson-Mehl-Avrami model at the eutectic point and autocatalytic reaction model at hypoeutectic and hypereutectic composition region. It indicates that the kinetic transition process is nucleation-growth type in PbSn melts. From diffusion viewpoint, the mechanism of autocatalysis has been discussed roughly, and explained the reason for the change of transition models. Through analysis to its mechanism, it will be beneficial for further understanding of the essence of LLST.

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