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Temperature-induced liquid–liquid transition process in eutectic Pb–Sn melt explored from kinetic viewpoint

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Abstract

Up to now, there have been few studies of the temperature-induced liquid–liquid structure transition (LLST) kinetics for atomic systems. In this paper, through isothermal and heating experiments, we have investigated the kinetics of the LLST process in Pb–Sn61.9 wt% melt by measuring the electrical resistivity and heat flux. The time evolution of the heat flux and electrical resistivity can be described by the Johnson–Mehl–Avrami model with an Avrami exponent of 3.87, which is an indication of nucleation-growth-type ordering of the nonconserved order parameter. What is more, we have calculated the reaction rate constant K_T and apparent activation energy ΔE , and deduced the reason for the characteristics of temperature-induced LLST. The result of this research could be beneficial for a further understanding of the essence of LLST.

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

1. Introduction

In recent years, evidence of structural transition in liquids has been suggested in many reports [1–7]. After pressure-induced LLST was verified via diffraction reported in liquid phosphorus [8], it is noteworthy that an anomalous temperature-induced LLST far above the liquidus at ambient pressure has been discovered in more and more binary melts, e.g. In–Sn, Pb–Sn, Al–Cu and In–Sb [9–15]. Together with pressure-induced LLST, the temperature-induced LLST presents a challenge to our conventional picture of liquids as entities with a continuously varying averaged structure, and enriches the phenomenology of the liquid state. For molecular liquids, there have been detailed studies of the kinetics of the liquid–liquid transition [16–18]. However, for atomic systems, research on temperature-induced LLST has mainly been focused on finding the pertinent transition phenomena in liquid elements or alloy

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systems, while the transition mechanism and characteristics have been little studied. In this paper, we will attempt to explore these problems from a kinetic viewpoint.

In a previous study, we investigated the existence of LLST in the eutectic Pb–Sn61.9 melt through internal friction experiments [9]. For further study of the transition process, isothermal and heating experiments were conducted using the dc four-probe resistivity method and the differential thermal analysis (DTA) method. Kinetic phenomena have been observed clearly in the LLST process. The time evolution of the heat flux and electrical resistivity has been found to be well fitted by the Johnson–Mehl–Avrami model with an Avrami exponent of 3.87. During heating experiments, with an increase in the heating rate the whole transition region correspondingly moves to higher temperatures. Using Kissinger's equation, we calculated the apparent activation energy, ΔE , at the temperature at which the transition begins. Moreover, the mechanism and characteristics of the transition process were also discussed. We believe that the present results for liquid Pb–Sn61.9 could be helpful to understanding the characteristics and mechanism of temperature-induced LLST in other binary melts.

2. Experiments and results

As a structure-sensitive physical quantity, electrical resistivity could be used for studying the liquid structural change. In this paper, we investigate the electrical property of liquid Pb–Sn61.9 melt using the dc four-probe method, and DTA was also employed in isothermal experiments (PYRIS DIAMOND TG/DTA). Weighted amounts of 99.99%-pure Sn and Pb were melted at 400 °C for over 30 min, then poured into measuring cells and cooled to room temperature for the following experiment. Measuring cells, 3.38 mm in diameter, are made from silica glass. The thermal expansion of the silica glass was so small that variation in 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 using a Keithley-2182 nanovoltmeter, while a constant current of 500 mA was supplied from a PF66M sourcemeter. The experimental details and equipment have been described elsewhere [19]. The resistivity measurements were carried out in purified argon media to protect the sample from oxidation.

2.1. Isothermal experiments

Isothermal experiments have been made on Pb–Sn61.9 melt held at different temperatures. Samples were heated rapidly to 773 and 888 K (about 300 K min⁻¹) then held for 18 and 6 h, respectively. The curves of resistivity versus time ($\rho-t$) and the results of the DTA experiment are recorded in figures 1 and 2.

In figure 1, held at 773 K for 18 h, the resistivity of the Pb–Sn melt is almost unchanged, which reflects that the liquid structure is steady at low temperatures and that influencing factors such as composition segregation can be neglected. But in figure 2(a), an S-shaped change in the $\rho-t$ curve occurs after holding at 888 K for 75 min. Through the tangent method, we selected t_0 and t_e as the transition beginning time and ending time, respectively. Correspondingly, an endothermic peak is also clearly observed in the curve of the DTA experiment. This indicates the existence of a liquid structure change in Pb–Sn melt (figure 2(b)). Moreover, there are small humps, in both the resistivity and DTA curves, present in figure 2. We assume that this is a pre-transition phenomenon.

2.2. Heating experiments

In addition to the isothermal experiment, a heating experiment was also performed on the Pb–Sn61.9 melt. Samples were heated continuously from room temperature to 1573 K at different

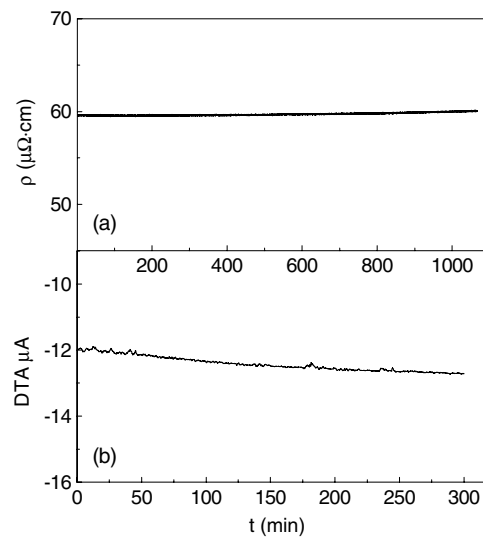


Figure 1. Pb–Sn61.9 isothermal experiments held at 773 K: (a) curve of resistivity versus time and (b) result of DTA experiment.

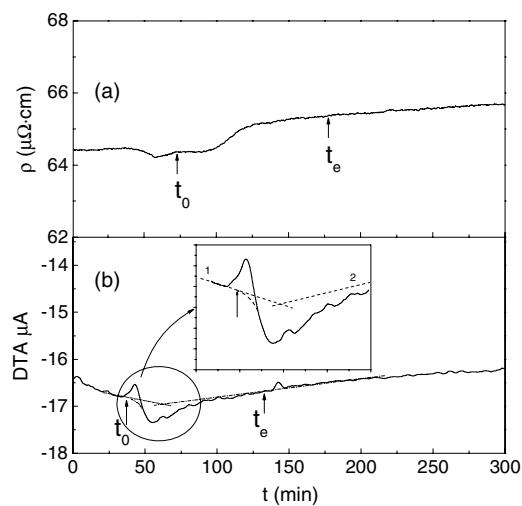


Figure 2. Pb–Sn61.9 isothermal experiments held at 888 K: (a) curve of resistivity versus time and (b) result of DTA experiment.

heating rates: 2, 5, 7.5, 10, 12.5 and 15 K min⁻¹ (see figure 3 and table 1). Obviously, kinetic phenomena were observed in the transition process.

With an increase in the heating rate, both the transition beginning point (T_0) and the transition ending point (T_h) move to higher temperatures, and also the temperature region ($\Delta T = T_h - T_0$) becomes narrower (figure 4). As an atomic diffusion and rearrangement process, a liquid transition needs enough time for structural change, so the heating rate can affect T_0 and T_h greatly. Furthermore, in figure 4 it can be seen that the variations in amplitude of T_0 , T_h and ΔT decrease with an increase in heating rate, which means that the heating rate

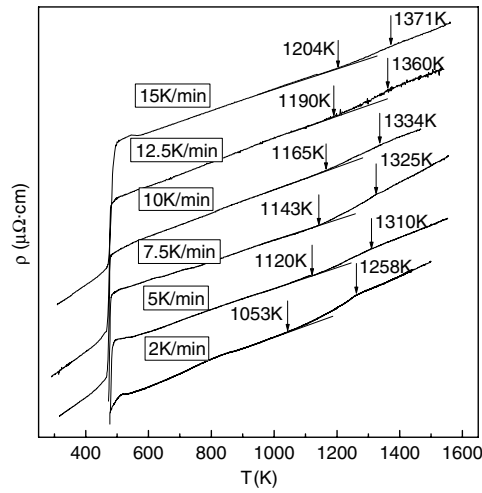


Figure 3. Resistivity versus temperature curve of Pb–Sn61.9 at different heating rates.

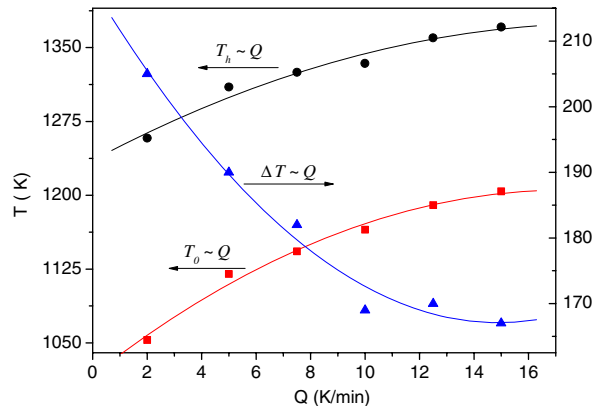


Figure 4. Curve of T_0 , T_h and ΔT versus heating rate Q .

Table 1. Pb–Sn61.9 starting temperature, ending temperature and temperature range of L–L structure transition.

	Q (K min ⁻¹)					
	2	5	7.5	10	12.5	15
T_0 (K)	1053	1120	1143	1165	1190	1204
T_h (K)	1258	1310	1325	1334	1360	1371
ΔT (K)	205	190	182	169	170	167

cannot affect the transition process in an unlimited way. All these reveal the kinetic nature of temperature-induced LLST.

3. Discussion

Through electron and neutron diffraction experiments, Dahlborg *et al* investigated the eutectic Pb–Sn melt during heating and subsequent cooling [15]. In the Pb–Sn initial

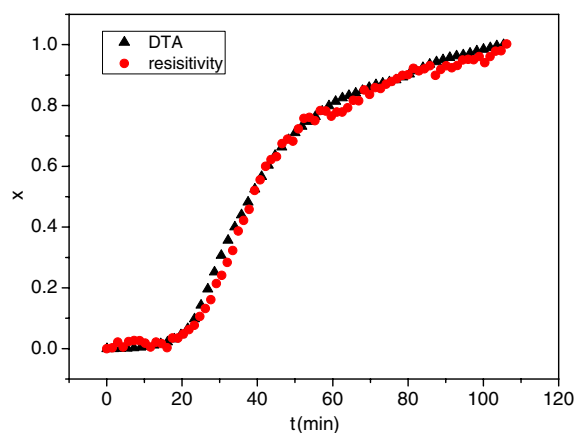


Figure 5. Curve of structure transition fraction versus time that Pb–Sn61.9 is held at 888 K.

microheterogeneous state formed after melting, microdomains of different sizes of the two families have been seen, which are enriched in one of the components. With a temperature increase above 500 °C, the microdomains either break up or disintegrate into smaller ones. The melt becomes a true solution, a completely mixed liquid state. The results show that the melt undergoes irreversible structural transformation from the initial microheterogeneous state (phase I) to the true solution state (phase II). This testifies to the existence of a liquid–liquid transition high above the liquidus and indicates that the liquid–liquid transition is not a phase separation. In our previous study, we also deduced the transition mechanism in Pb–Sn melts from the standpoint of thermodynamics, which could be described simply as $L'(Pb) + L''(Sn) \rightarrow L(Pb-Sn)$ [9]. From the above analysis, it could be seen that Pb–Sn LLST is a kinetic process with a new phase forming and an old phase disappearing, in which local atomic rearrangement in atomic clusters plays the main role.

During the transition process, the time evolution of the structure transition fraction (x) could be deduced from figure 2. For the DTA experiment, with tangent 1, 2 as the baseline, x is given by $x = A_{(t)}/A_{(tot)}$, where $A_{(t)}$ is the area encircled by the DTA curve and baselines at time t , and $A_{(tot)}$ is the total area from t_0 to t_e . The $x-t$ curve was plotted in figure 5 (black dashed line).

With further conversion and analysis, it is found that this transition process fits the J–M–A transition model well, which can be described as follows:

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

where K_T is the reaction rate constant and n is the Avrami exponent. With $\log \log 1/(1-x)$ and $\log t$ as variants, the curve is plotted in figure 6 ($x = 0.1-0.9$). It stays approximately linear when $x < 0.8$, and then deviates greatly from linear. $\ln K_T$ is calculated as -15.38 , the value of which reflects the transition speed and is much smaller than that of a normal solid-state phase transition. The linear slope n is 3.87, which is an important parameter reflecting a different transition pattern. It indicates that the Pb–Sn61.9 LLST process is of nucleation-growth type, and is similar to a solid polymorphic transition process. Liquid phase II is nucleated randomly and homogeneously with a nucleation rate decreasing with time, and grows with a constant growth rate. Kurita and Tanaka have investigated the liquid–liquid transition in liquid triphenyl phosphite, and a nucleation-growth type process has also been found in the time evolution of the heat flux annealed between 215.5 and 223 K [20].

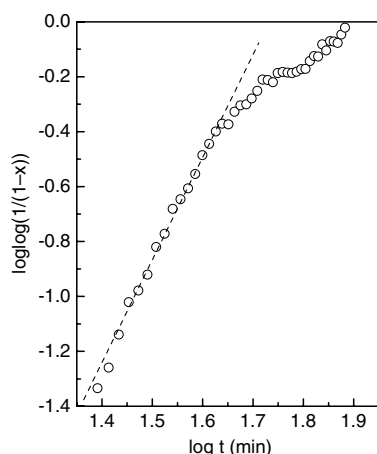


Figure 6. Curve of $\ln(\frac{1-x}{x})$ versus time in Pb-Sn61.9 held at 888 K.

For a nucleation-growth-type transformation having a droplet structure, x could be calculated by $x = (\rho_t - \rho_0)/(\rho_e - \rho_0)$ for the resistivity experiment as well, 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 . The $x-t$ curve (figure 5, red dashed line) deduced from the $\rho-t$ curve is consistent with that deduced from the DTA experiment. This testifies to the validity of the above-mentioned analysis based on the J-M-A transition model, and the reliability of the electric resistivity method used for investigating the liquid structure transition.

From previous study, it can be seen that a much wider transition temperature region and longer transition time are extrinsic characteristics of temperature-induced LLST, which shows that its transition speed is slower than that of a normal structure transition. Correspondingly, the calculated K_T (reaction rate constant) is some orders of magnitude smaller than that of a normal solid-state phase transition. For example, in the heating experiment, the Pb-Sn liquid transition temperature region can reach 190 K at 5 K min^{-1} (table 1) and, when the temperature is held at 888 K, the total transition time is 107 min (see figure 5). For a nucleation-growth type transition, both the nucleation rate (I) and the growth rate (u) of the new phase are important factors influencing the transition speed. But in a liquid structure transition process, only I plays a main role and u has little contribution to the transition speed, which is because atomic clusters have almost no chance of growth due to the long-range disorder of the liquid structure. This is why the transition speed of temperature-induced LLST is much slower than that of a normal structure transition.

For the J-M-A transition model, Kissinger's equation can be used to evaluate the kinetics of the transition process. With various heating rates, the apparent activation energy at the transition starting temperature can be calculated, which is the energy needed to overcome the energy barrier of the structure transition. The equation is described as [21]:

$$\ln \frac{T^2}{Q} = \frac{\Delta E}{RT} + A \quad (2)$$

where T is the transition starting temperature, Q is the heating rate, R is the gas constant, A is a constant, and ΔE is an apparent activation energy. Equation (2) can be considered to be a linear equation with $\ln(T^2/Q)$ and $1000/T$ as variants. Based on heating experiment data (table 1), we can get a linear line (figure 7) with a slope ($\Delta E/R$) of 14.80, and therefore ΔE is calculated to be $122.54 \text{ kJ mol}^{-1}$. This value is smaller than that of a normal solid structure

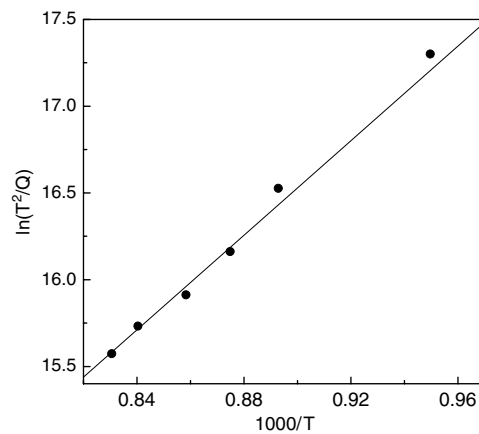


Figure 7. Curve of $\ln \frac{T^2}{Q}$ versus $\frac{1000}{T}$.

transition, which means that mainly localized atomic structure rearrangement occurs in the LLST process.

4. Conclusion

Through isothermal and heating experiments, the kinetic property of the Pb–Sn61.9 LLST process has been well studied. We have found that, fitted by the J–M–A transition model, the time evolution of the heat flux and resistivity is of nucleation-growth type. The Avrami exponent n and the reaction rate constant $\ln K_T$ are calculated to be 3.87 and -15.38 , respectively. The value of n reflects that the LLST process is similar to a solid polymorphic transformation process, in which the nucleation rate decreases with time. We have also discussed the reason for the characteristics of temperature-induced LLST, and calculated the apparent activation energy ΔE at the transition's beginning temperature using the Kissinger equation. Our work suggests that kinetic behaviour may exist not only in the Pb–Sn61.9 liquid structure transition but also in the liquid structural transitions of other alloy systems.

Acknowledgments

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