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Structure change of Pb melt

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Abstract

Using viscometer, densitometer, magnetic susceptibility device, DSC and X-ray diffractometer for high temperature (XRD), the Pb melt has been investigated between 800–1200 K. Anomalous changes in the physical properties were found near the same temperature. X-ray diffraction shows that the size of clusters in the low temperature zone is much larger than that in the high temperature zone. It is presumed that some solid-like structure occurred at the anomalous point of the physical properties during the cooling process.

Keywords: Pb melt; Viscosity; Density; Magnetic susceptibility

1. Introduction

Research on the structure of liquid metals has attracted more attention recently. It is one of the hottest topics in both technical and theoretical fields of condensed matter physics [1–3]. It is important to obtain the structural information of the melt at high temperatures above melting point for us to understand the nature of liquid metals. Studies recently show that there are discontinuous structural changes induced by temperature in the liquid. More significantly, liquid–liquid phase transitions have been proved, experimentally and theoretically, to occur in some liquid metals and alloys. Su-Juan Cheng studied the structural changes of In melt by viscometer and X-ray diffractometer [4]. Sastry found the liquid–liquid phase transition in supercooled silicon [5]. The structural changes in Pb–Sn [6], Pb–Bi [7], In–Sn [8] alloys have been proved using internal friction technique. From the results of magnetic susceptibility, Sidorov studied the structural transformations of liquid iron-based melts and plotted the lines of structural transformation in the liquid phase [9]. Gui studied viscosities of hypoeutectic and hypereutectic Al–Si alloy melt. He presumed that there are three kinds of structure zones in Al–Si alloy melts for the sudden changes in structure [10]. Buldyrev developed the models for a liquid–liquid phase transition with molecular dynamics simulations [11].

The physical properties and structure of pure liquid Pb has attracted considerable attention in recent years because the Pb melt cannot be described using the random hard-spheres-packing model usually employed for simple liquid metals [12]. In this work, some primary physical properties of the Pb melt, such as viscosity, density and magnetic susceptibility have been measured, at about 800–1200 K. DSC and X-ray diffraction are also used to study the structure of Pb melt.

2. Experimental

The metal used in this work is 99.999 wt% Pb.

A torsional oscillation viscometer for high-temperature melts is employed to measure the viscosity of Pb melt. The principle parameters of the viscometer are as follows: repetition rate ±5%; temperature precision ±3 K; highest measuring temperature 1773 K. The sample was melted in a graphite crucible using a medium frequency induction furnace and cast ingots in a graphite mould. It was cast into a cylindrical sample, 27 mm in diameter and 50 mm in height. An Al_2O_3 vessel filled with the sample is suspended on a molybdenum wire. The vessel is put in torsion oscillation and the motion damped gradually with the absorption and dissipation of frictional energy in the

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Pb melt. The oxygen was removed from the vessel by applying a vacuum of 0.02 Torr and then filled with high purity argon (99.9% Ar) at a pressure above atmospheric pressure to prevent oxidation of the melt. The sample was heated to 1163 K at the heating rate of 4 K/min. To ensure the temperature of the samples was stabilized, it is held for half an hour before each measurement. The measurements at each temperature were carried out four times and the average values were used. The error of viscosity measurement is less than 4% in different temperature.

The device to measure magnetic susceptibility was designed by our group. The principle of the device is the law of electromagnetic induction. The device is consists of two coils with ferroamorphous cores in the shape of a ring with a slot. The sample was heated to liquid and placed into the slot of one core while another sample used as a reference was not heated and placed in the slot of the other core. A magnetic circuit is composed of the coils and samples. The magnetic susceptibility variations of the sample will affect the magnetic resistance of whole magnetic circuit, and then the magnetic susceptibility variations of the sample can be measured. The sample was put in a quartzose pipe, which is heated to 1273 K in an argon atmosphere, and then the pipe was placed in the slot of core. The temperature of sample was measured by Raynger 3i infrared radiation thermometer and recorded by a computer at the same time.

Density is measured by the Archimedean method. The principle of this method is the buoyancy of solids in liquid. A graphite pin with the weight of W_1 is hung by molybdenum wire. The weight of the pin in liquid is W_2. The density of liquid can be expressed by the following equation

$$\rho = (W_1 - W_2)/V, \tag{1}$$

where V is the volume of the pin in the liquid. The columned sample which was $\varnothing\ 50 \times 55$ mm was put in a graphite crucible with argon atmosphere. The measurements were carried out five times at each temperature and the average was used. The error of the measurement of density is not exceeding 0.5%.

The θ–θ liquid metal X-ray diffractometer used in this work was made by Metal Physics Institute of Ukraine National Academy. The wave length is $\lambda = 0.071$ nm (Mo Kα radiation), the accuracy of the angle is 0.001° and the range of scanning angle (2θ) is 5–90°. The sample was put in an Al_2O_3 crucible and heated to 1300 K, and held for half an hour. Then the sample was measured during the cooling process.

3. Results and discussion

The temperature dependence of dynamic viscosity (η) can be described by the Arrhenius equation [13]

$$\eta = A\exp(\varepsilon/kT) = \frac{h}{\nu}\exp(\varepsilon/kT) \tag{2}$$

where A is a constant; η is the dynamic viscosity; h is the Planck constant; k is the Boltzmann constant; T is the absolute temperature; ν is the volume of flow unit; and ε is the activation energy of viscosity.

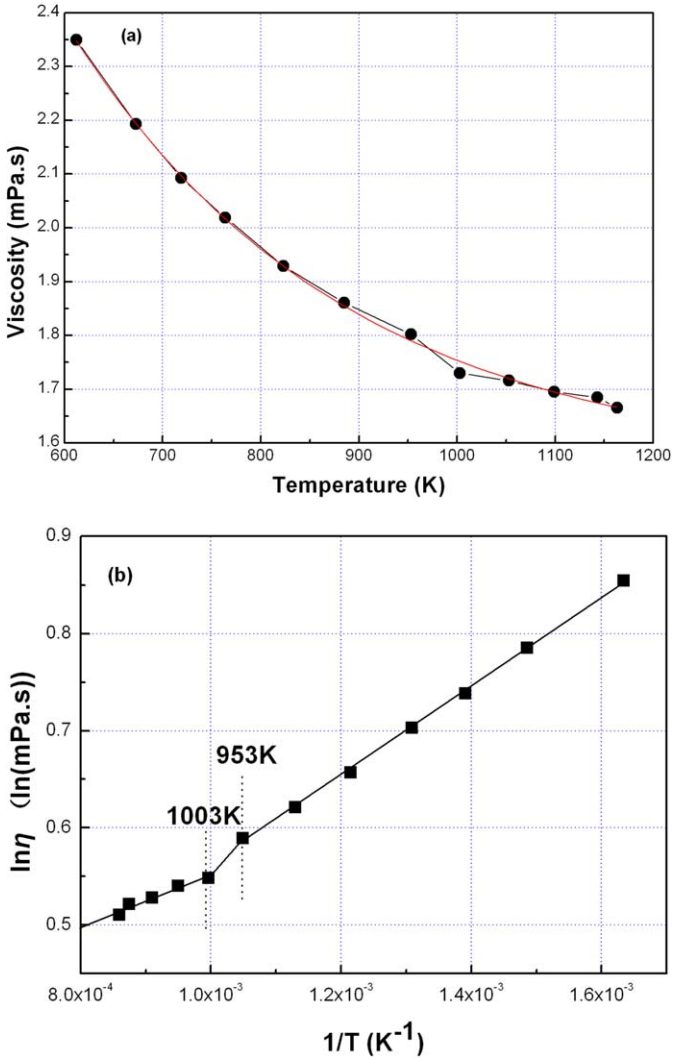

Fig. 1. (a) The viscosity (η) variations of the Pb melt with temperature during cooling process. (b) The logarithmic viscosity ($\ln\eta$) versus $1/T$ of the Pb melt.

Fig. 1(a) shows the temperature dependence of the dynamic viscosity of the melt during the cooling process. It can be seen that the viscosity increases when temperature decreases. Exponential decay is applied to the viscosity to verify the validity of the following equation

$$\eta = \eta_0 + A_1\exp\bigl(-(t - t_0)/B_1\bigr) \tag{3}$$

where t is temperature (K); A_1 and B_1 are constants relating to the type and composition of the metals. The temperature dependence of the viscosity of the melt generally obeys the exponential relationship but not rigorously, which is similar to the results in the second step calculated by Morioka [14]. For better understanding of the change of viscosity of the melt, the logarithm is taken for both sides of Eq. (2), resulting in Eq. (4)

$$\ln\eta = \ln A + \varepsilon/kT. \tag{4}$$

Fig. 1(b) shows the curve of $1/T$ versus $\ln\eta$ of the melt. It is obvious that there is a discontinuous point in the temperature range of 953–1003 K. This point divides the curve into two segments: the low and high temperature zones, which can be seen