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Atomic structure and physical properties of liquid Pb–Bi alloys

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Abstract

The atomic structure and physical properties (dynamic viscosity, electrical conductivity, and thermopower) of liquid Pb–Bi alloys have been investigated in a wide temperature range. Gradual and reversible changes of the physical properties during heating and cooling of the Pb–Bi liquid alloys have been observed. No drastic structural transformations or atomic rearrangement with temperature variation have been found.

1. Introduction

During recent years, considerable attention has been given to a reassessment of the physics and engineering fundamentals of nuclear reactors, especially to design and implementation of fast reactors and accelerator driven systems (ADSs) [1]. One of the crucial tasks is the choice of an appropriate material for the target. In this connection, Pb–Bi alloys have come under the scrutiny of science. Bi–Pb melts are chemically inert with air and water. They have high boiling temperatures, low vapour pressure, and good heat transfer characteristics. Besides, bismuth–lead alloys have a satisfactory neutron production sufficiency. Due to all these factors, liquid Bi–Pb eutectic ($Pb_{44.1}Bi_{55.9}$) with the melting point of $\sim$125 °C is considered as the prime candidate to be applied in the Spallation Neutron Sources (SNSs) and ADSs as the target material and the main component of the heat removal system. At present, the megawatt pilot experiment (MEGAPIE), an international project to design, build and operate a liquid metal spallation neutron target (lead–bismuth eutectic) supported by nine institutes and the European Union, is being carried out at the Spallation Neutron Source, Paul Scherrer Institute, Switzerland [2]. Knowledge of the physical properties of liquid Pb–Bi alloys, and those of eutectic composition especially, is thus of high scientific and practical importance.

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A post-melting anomaly of Pb–Bi alloys observed by the internal friction technique has been reported on recently in [3]. An unusual temperature dependence of the internal friction was found. The measurements performed on the three liquid alloys containing 30 wt% Bi, 56.1 wt% Bi and 20 wt% Bi showed that the internal friction decreases continuously after melting up to a temperature of about 500–550 °C and then it starts to grow very strongly, reaching a peak at around 600–650 °C. As the temperature is further increased the internal friction drops, and it achieves values which could probably (our supposition) be extrapolated from the experimental data measured in the low-temperature region. Besides, an exothermic peak in the DSC curve of the $Pb_{70}Bi_{30}$ alloy was observed at about 660 °C, and afterwards the specific heat increased with temperature. This was interpreted in [3] as evidence of structural changes taking place in the molten alloys as a function of temperature.

The post-melting anomaly reported in [3] requires investigations of the Pb–Bi liquid alloys both from purely scientific and applied points of view, especially taking into account the application of the lead–bismuth eutectic in SNSs and ADSs where thermophysical properties and viscosity play a very important role. In this paper we present the results of the x-ray diffraction study of liquid Pb–Bi liquid alloys as well as the experimental data of the electrical conductivity, thermopower and dynamic viscosity measured in a wide temperature range.

2. Experimental details

2.1. X-ray diffraction measurements

The structure of Pb–Bi liquid alloys has been investigated with a high-temperature θ–θ diffractometer. Mo Kα-radiation diffracted by the sample was selected by a focusing graphite monochromator. The scattered intensity was measured with a scintillation detector with a pulse height analyser. The magnitude of the diffraction vector $Q = 4\pi \sin\theta/\lambda$, where θ is half the scattering angle and λ is the radiation wavelength, ranged from 1 to 10 Å^{-1}. The scanning step was 0.05 Å^{-1} for $Q \leqslant 5$ Å^{-1} and 0.1 Å^{-1} for $Q > 5$ Å^{-1}. The statistical error of counting at the 'tail' of the scattering curve did not exceed 3%.

The temperature of the samples was controlled by a regulator and maintained within ± 1 K of a set-point during an x-ray diffraction experiment. The temperature reading was calibrated by measuring the melting points of In, Sn, and Ag.

The samples were prepared by melting from granules of Pb and Bi of 99.999% purity in evacuated quartz ampoules. In order to remove the oxide layers on the sample surface the following treatment was carried out. After setting up a sample in the chamber it was evacuated to better than 5×10^{-4} mbar and filled with a gas mixture of 90% Ar and 10% H_2. The sample was heated to 830 °C, kept there for 10–15 min, and cooled down to room temperature. Afterwards, the chamber was evacuated again to $\sim 5 \times 10^{-4}$ mbar and filled with Ar–10% H_2 mixture up to $\sim$1 bar. Then the sample was heated to the temperature chosen for the investigation.

The x-ray diffraction intensities measured in arbitrary units were converted into coherent scattering intensities per atom in electron units using the generalized Krogh-Moe–Norman method [4, 5] and then the Faber–Ziman [6] structure factors were obtained.

2.2. Viscosity measurements

The measurements of the viscosity were carried out using a computer-controlled oscillating-cup viscosimeter [7]. Using the modified Roscoe equation, the dynamic viscosity, η, was calculated from the logarithmic decrement and the period of oscillations [8]. The needed density values were calculated from the densities of the constituents [9].

The appropriate amounts of Pb and Bi (99.999% of purity) were initially melted from granules in evacuated and sealed quartz ampoules. The samples, having an absolute mass of about 95 g, were accurate in composition to ±0.02 wt%. Each sample was weighed before and after the measurements, and no loss of mass was observed. Cylindrical boron nitride crucibles (20 mm inner diameter, 40 mm height) were used. As in the case of the diffraction investigations, the viscosity measurements were performed in an atmosphere of 90% Ar–10% H_2 after initially pumping out the working volume of the furnace to about 5×10^{-3} mbar. A homogeneous temperature field ±0.3 K cm^{-1} in the range of absolute values up to 800 °C was created inside a furnace. The temperature was measured with a Pt/PtRh thermocouple arranged just below the crucible. The viscosity values were obtained with an accuracy of ∼5%.

2.3. Electrical conductivity and thermopower measurements

The measurements of the electrical conductivity and thermopower were carried out by a contact method in accordance with the four-point scheme as described elsewhere [10]. The samples were contained in the measuring cells manufactured of boron nitride ceramics in the form of vertical cylinders with an operating cavity height of 60 mm. Six graphite electrodes, two for the current and four for the potential measurements, were inserted into the wall of the container along its vertical axis. The potential electrodes were provided with WRe-5/20 thermocouples. This permitted simultaneous determination of the temperature as well as measurement of the electrical conductivity and thermopower in one run. Moreover, the cell construction allowed analytical elimination of jamming and noise signals arising due to contact wires as well as a systematic device deviation.

Pure Pb and Bi were melted in evacuated and sealed quartz ampoules. A sample was inserted in the cell and set up in a high-pressure vessel. The experiments were performed under Ar gas atmosphere. The resultant error of the electrical conductivity is ∼2%, and that of the thermopower is ∼5%.

3. Experimental results and discussion

Pure Pb and Bi and six Pb–Bi alloys situated between them and distributed relatively equally on the entire concentration range were selected for structural investigations. The experimental structure factors of the liquid Pb–Bi alloys measured at the constant temperature of 350 °C are plotted in figure 1. They are in agreement with earlier x-ray diffraction investigations on molten Pb–Bi alloys [11]. The concentration dependences of the position and the height of the first maximum of the structure factors are shown in figure 2. The position and the height of the first maximum of $S(Q)$ change gradually with composition. A remarkable feature is observed only on the right-hand side of the first maximum of the structure factors. A shoulder, characteristic for liquid Bi, starts to develop there when Bi content is increasing.

Figures 3 and 4 present the experimental structure factors of the $Pb_{70}Bi_{30}$ and $Pb_{44.1}Bi_{55.9}$ alloys obtained at different temperatures up to 750 °C. It is seen that the intensities of the maxima and minima vary but their positions as well as the general shape of the functions do not change in a wide temperature interval. Besides, no differences occur between the structure factors of the alloy measured near the liquidus line just after melting and after cooling the samples from 825 °C. This shows that there is no structural rearrangement on the micro-level due to heating and cooling of the Pb–Bi liquid alloys.

There could however arise a question concerning a relaxation phenomenon. Indeed, the duration of an x-ray diffraction experiment is rather long (3–6 h), so that it is not possible to follow any structural change if it takes place in a short period of time. In this connection, the temperature dependences of the electrical conductivity, thermopower and dynamic viscosity,

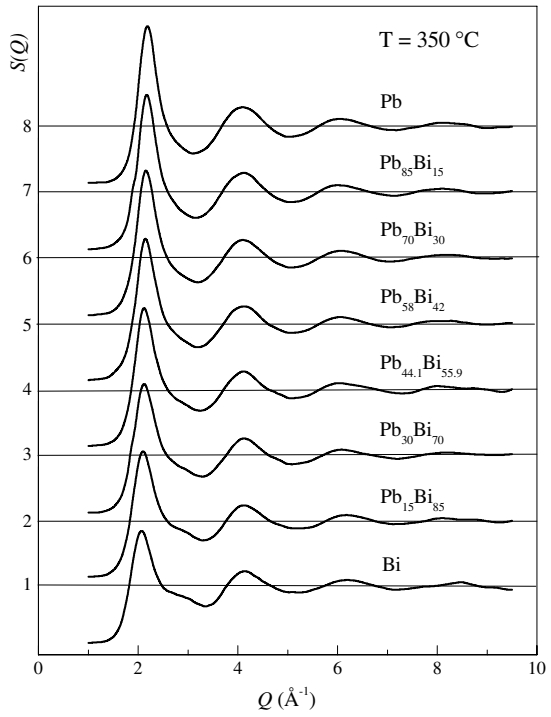

Figure 1. Experimental structure factors of the Pb–Bi liquid alloys at 350 °C.

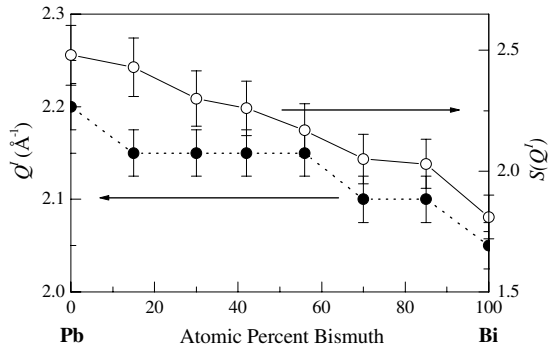

Figure 2. Composition dependences of the position Q^{I} and the height $S(Q^{\mathrm{I}})$ of the main peak of the structure factors for liquid Pb–Bi alloys (lines are guides for the eyes).

which are very sensitive to any structural arrangement that may take place in a melt, have been measured.

Figures 5 and 6 show the temperature dependences of the electrical conductivity and thermopower of the liquid $Pb_{70}Bi_{30}$ and $Pb_{44.1}Bi_{55.9}$ alloys. They do not reveal any unexpected temperature behaviour. The electrical properties of the investigated melts vary linearly with temperature within the experimental error. A good agreement between the heating and cooling curves for the eutectic composition has been observed. Besides, the eutectic alloy was heated and cooled several times with different rates. It has been established that the variation of the process velocity does not affect noticeably the electrical conductivity and thermopower temperature dependences.

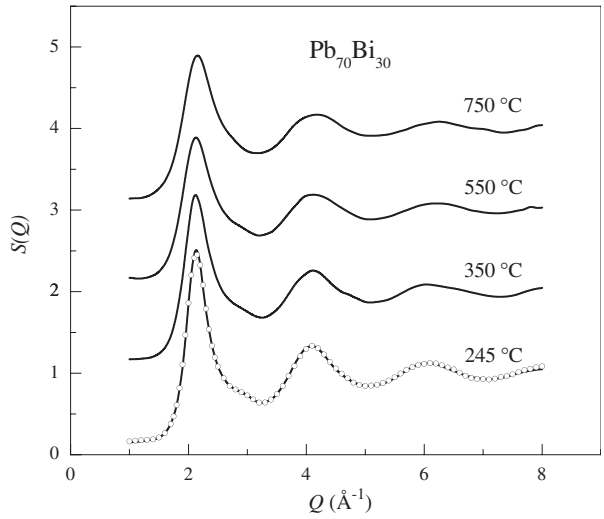

Figure 3. Experimental structure factors of liquid $Pb_{70}Bi_{30}$ alloy: full curves—measured after cooling from 825 °C; open circles—measured after melting the sample.

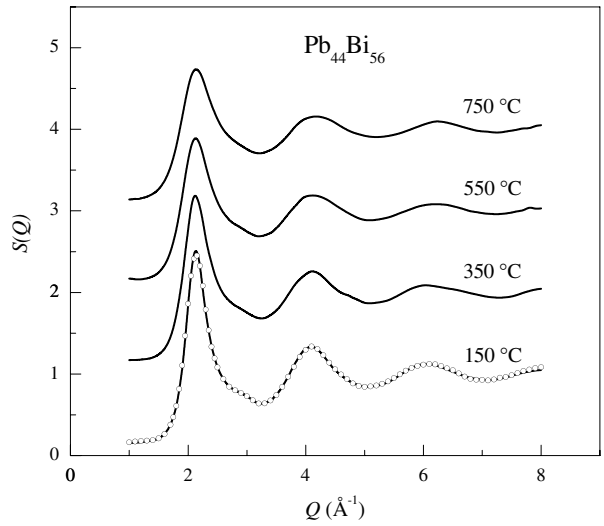

Figure 4. Experimental structure factors of liquid $Pb_{44.1}Bi_{55.9}$ alloy: full curves—measured after cooling from 825 °C; open circles—measured after melting the sample.

The temperature dependences of the dynamic viscosity for the $Pb_{44.1}Bi_{55.9}$ and $Pb_{70}Bi_{30}$ alloys are plotted in figures 7 and 8. The absolute values of the viscosity measured during heating and subsequent cooling of the samples are virtually coincident. It is also seen from figures 7 and 8 that the temperature dependences of the viscosity for the $Pb_{44.1}Bi_{55.9}$ and $Pb_{70}Bi_{30}$ alloys are rather well described by the Arrhenius equation:

$$\eta = \eta_0 \exp\left(\frac{E_a}{RT}\right), \tag{1}$$

where η is the dynamic viscosity (mPa s), R is the gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), E_a is the flow activation energy (J mol^{-1}), and η_0 is a constant

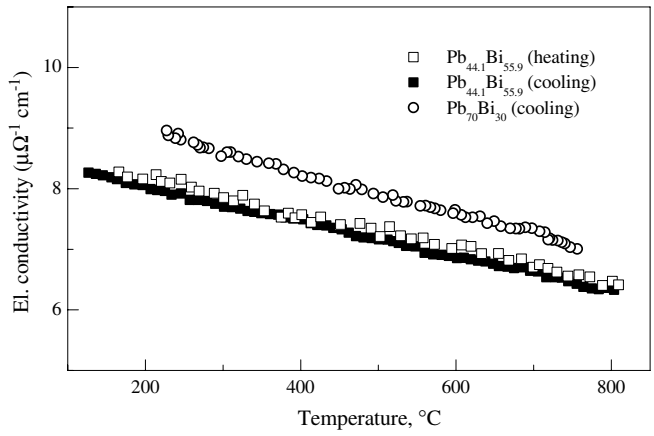

Figure 5. Temperature dependences of the electrical conductivity for liquid $Pb_{70}Bi_{30}$ and $Pb_{44.1}Bi_{55.9}$ alloys.

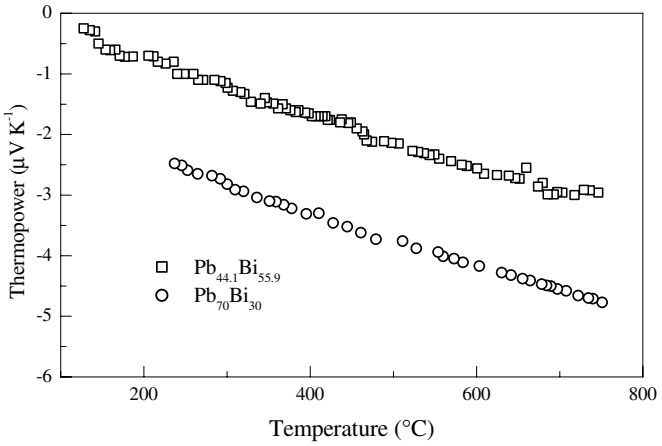

Figure 6. Temperature dependences of the thermopower for liquid $Pb_{70}Bi_{30}$ and $Pb_{44.1}Bi_{55.9}$ alloys.

(mPa s). The activation energy of viscous flow determined from the experimental values of the dynamic viscosity measured during cooling equals ∼7.13 kJ mol^{-1} for $Pb_{70}Bi_{30}$ liquid alloy, and ∼7.92 kJ mol^{-1} for liquid $Pb_{44.1}Bi_{55.9}$ alloy.

4. Conclusions

X-ray diffraction study of liquid Pb–Bi alloys in a wide temperature interval has shown that the atomic structure changes gradually with the temperature and all changes taking place during heating are completely reversible during subsequent cooling of the melts. This is confirmed by the experimental investigations of various structure-sensitive physical properties of $Pb_{70}Bi_{30}$ and $Pb_{44.1}Bi_{55.9}$ liquid alloys. It has been found that the absolute values of the dynamic viscosity, electrical conductivity, and thermopower measured in the course of heating and subsequent cooling of the samples are coincident; observed fluctuations are within the

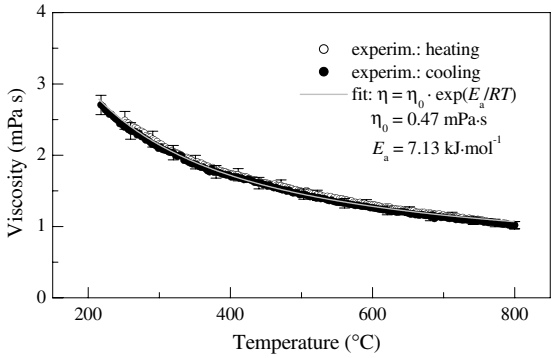

Figure 7. Temperature dependences of the viscosity for liquid $Pb_{70}Bi_{30}$ alloy.

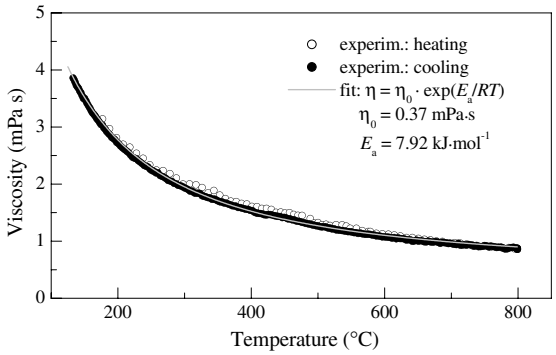

Figure 8. Temperature dependences of the viscosity for liquid $Pb_{44.1}Bi_{55.9}$ alloy.

experimental errors. It is noteworthy that the dynamic viscosity of the investigated $Pb_{70}Bi_{30}$ and $Pb_{44.1}Bi_{55.9}$ liquid alloys decreases gradually with increasing temperature and no unusual behaviour at high temperatures has been observed.

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