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Crystallization and relaxation phenomena in the bismuth–lead eutectic

R.A. Khairulin[a,*], K.M. Lyapunov[a], A.G. Mozgovoi[b], S.V. Stankus[a], P.V. Ulyusov[c]

[a] *Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences, Kutateladze 2, Novosibirsk 630090, Russia*

[b] *Scientific Association for High Temperatures, Russian Academy of Sciences, Izhorskaya street 17/19, Moscow 125412, Russia*

[c] *Novosibirsk State University, Pirogova 2, Novosibirsk 630090, Russia*

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Abstract

The thermal properties of the solid and liquid bismuth–lead eutectic (44.6 wt.% Pb) have been investigated by a γ-ray attenuation technique over the temperature range from 293 to 750 K. New data on the temperature dependences of the solid and the melt densities have been obtained. The density change during the solid–liquid transition has been directly measured for the first time. The effect of the solid density relaxation has been detected and studied. A model has been proposed, which explains the observed phenomenon.

Keywords: Bismuth–lead eutectic; Solid; Melt; Density

1. Introduction

The molten bismuth–lead eutectic is used as heat-transport medium in nuclear power. In particular, this melt is employed in some types of ship reactors [1]. The density and thermal expansion of the liquid eutectic have been repeatedly studied [1–3]. However, we have not found in the literature any data on the changes of the volume properties on melting–crystallization. Meanwhile, these data are essential for a prediction of the heat carrier behaviour during a start-up of a coolant circuit as well as in an emergency accompanied by melt solidification. In this connection, the aim of the present work was a comprehensive experimental study of the thermal properties of the eutectic in both solid and liquid states including the region of the phase transition.

2. Experimental details

The investigation of thermal properties of the bismuth–lead eutectic was performed by a γ-ray attenuation technique. The advantage of this method is its universality and, in particular, the possibility of direct measurement of the density changes during the solid–liquid phase transition. Details of the experimental equipment and procedures have been described elsewhere [4,5]. For the γ-ray source, we used the ^{137}Cs isotope having an activity of 240 GBq and a quanta energy of 662 keV. A cell for the samples was made from stainless steel. It included a cylindrical crucible, 25 mm in internal diameter and 60 mm in height, and a cap with a thin-walled protective sleeve for the chromel–alumel thermocouple. The thermocouple calibration was checked against the crystallization points of pure tin and antimony. The deviations of the measured solidification temperatures from reference data did not exceed 0.3–0.5 K. Before the experiments, the furnace of the γ densitometer was evacuated and filled with pure

* Corresponding author. Tel.: +7-3832-391541; fax: +7-3832-343480.
E-mail address: gamma@itp.nsc.ru (R.A. Khairulin).

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argon up to 0.1 MPa. The measurements of the sample density were conducted at a rate of heating–cooling of 2–3 K/min in the single-phase regions and not beyond 0.3 K/min over the range of the phase transformation. According to our estimate, the density measurement error did not exceed 0.2–0.3% at the top temperature of the experiments (750 K). The density of the samples at room temperature (both before and after high temperature experiments) was determined by the Archimedean method with an error of no more than 0.03%.

3. Results and discussion

The initial sample of the bismuth–lead eutectic was obtained from Leipunskii Institute of Physics and Power Engineering (Obninsk, Russia) in the form of an ingot weighing about 500 g. The ingot had a lead content of 44.6 wt.% (the literature data for the eutectic composition vary between 42.6 and 45.1 wt.% Pb [6,7]). The purity of the components was better than 99.998% (Pb) and 99.98% (Bi). It should be noted that the initial sample was synthesized about two years prior to our experiments.

Three pieces of about 100 g each were cut from different parts of the ingot. The measurements of the density of these pieces by the Archimedean method at room temperature yielded the following results: 10656.2 kg/m^3, 10658.2 kg/m^3, and 10656.1 kg/m^3. The scatter in the data (≤0.02%) was less than the density measurement error of the Archimedean method, that is, the initial ingot was sufficiently uniform in composition. The average of the three measurements (10656.8 kg/m^3) was taken as the density of the initial sample at room temperature.

The pieces cut out from the ingot were placed into the measurement cell. The cell was installed into the furnace of the γ densitometer, where the sample was melted and heated to 750 K. At this temperature, the melt was stirred thoroughly by a mechanical mixer. The melt homogeneity was checked by measuring the γ-ray attenuation in the sample at different heights. Then, in the course of cooling we measured the temperature dependence of the sample density in the liquid and solid states as well as the density change during the phase transition. The measurement results are presented in Fig. 1 (experiment 1, cooling). Notice that the sample crystallized practically at a constant temperature, $T_f = 397.9 \pm 0.3$ K, and the beginning of the melt solidification was preceded by minor supercooling. This temperature agrees with reference data on the eutectic melting point (398 K) [6] to within the limit of the estimated error. All these facts suggest that the sample composition is actually close to the eutectic one.

As is seen from Fig. 1, the density of the remelted solid sample has been found to be distinctly larger than the density of the original one. An extrapolation of the temperature dependence of the solid density obtained in the first experiment to 293 K gives a value of 10780 kg/m^3, 1.15 % larger than the initial value.

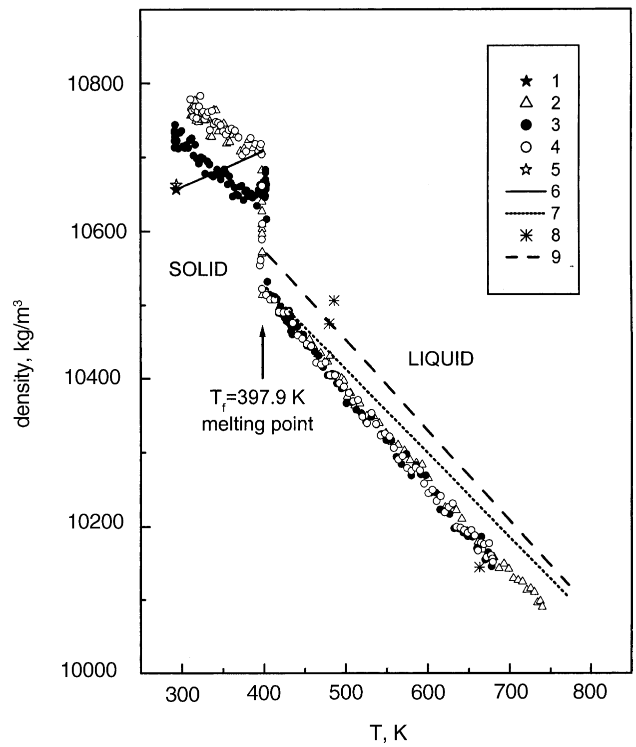

Fig. 1. The density of the bismuth–lead eutectic in solid and liquid states. Data of this work: (1) the density of original solid sample at 293 K measured before high-temperature tests; (2) experiment 1, cooling; (3) experiment 2, heating; (4) experiment 2, cooling; (5) the density of remelted solid sample at 293 K measured in about 4850 h after completion of high-temperature tests; (6) the temperature dependence of the density of equilibrium solid eutectic. Literature data on the melt density; (7) Alchagirov et al. [1] (44.6 wt.% Pb); (8) Been et al. [2] (43.5 wt.% Pb); (9) Nikol'skii et al. [3] (44.5 wt.% Pb).

In seven days after completion of the first experiment, we performed a second test with the same specimen. It turned out, that the solid density in this period fell markedly to 10730 kg/m^3 at 293 K and, respectively, it became closer to the density of the original eutectic. On heating (see Fig. 1: experiment 2, heating), the solid density decreased initially with increasing temperature. However, beginning with 390 K (∼7 K from T_f) the density began to increase, and, near the melting point, it practically attained the values obtained on the first cooling. The heating rate near the melting point was of about 0.3 K/min. In the liquid state, the results obtained on heating were in good agreement with the data of the first experiment. On cooling (see Fig. 1: experiment 2, cooling), the temperature dependences of the density of both solid and liquid agreed with the results of the first experiment, to within random error.

Eighteen hours after completion of the second experiment, the sample was removed from the cell and was cut into two parts (upper and lower) of roughly the same size. The densities of these pieces at 293 K measured by the Archimedean method were found to be equal to 10768.8 and