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Measurement of electrical conductivity of Pb–Bi alloys in the melting–solidification region

Yu. Plevachuk [a,*], V. Sklyarchuk [a], S. Eckert [b], G. Gerbeth [b]

[a] *Ivan Franko National University, Department of Metal Physics, 8 Kyrylo and Mephodiy Street, 79005 Lviv, Ukraine*
[b] *Forschungszentrum Dresden-Rossendorf, P.O. Box 510119, D-01314 Dresden, Germany*

Abstract

The electrical conductivity, $\sigma(T)$, of Pb–Bi alloys of eutectic and near eutectic compositions was investigated in the melting–solidification temperature region. The revealed discrepancies between the heating and cooling $\sigma(T)$ curves as well as a hysteresis observed in course of heating–cooling cycles suggest a metastable microheterogeneous structure of the Pb–Bi melts.

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1. Introduction

Among different heavy liquid metals the lead–bismuth alloys are considered as the main candidates for both the liquid metal spallation neutron source and the coolant of critical and subcritical reactors of a new generation [1–3]. Various target designs are under consideration including the set-up and instrumentation of related liquid metal loops [3–5]. Therefore, for the design of such targets it is of major practical interest to investigate the physical properties of eutectic and near-eutectic Pb–Bi alloys.

Such thermophysical properties as electrical and thermal conductivity, density, viscosity or specific heat, are of direct relevance for the thermohydraulic design of a Pb–Bi target and the related liquid metal loop. Several reviews of those data exist [6–10]. However, the discrepancy between the reported results, different investigated temperature ranges, and sometimes a very limited number of measuring points require new precise measurements in order to obtain reliable data on the temperature dependence of the above mentioned thermophysical properties over a wide temperature range.

Recently we reported new measurements on the electrical conductivity, thermoelectric power, viscosity, thermal conductivity, and surface tension of the eutectic Pb–Bi alloy in the temperature range between 400 and 1000 K [11]. It was found that the temperature dependence of the electrical conductivity (in units of $\Omega^{-1}\text{cm}^{-1}$) in the temperature range between the melting temperature T_m and 1000 K can be interpolated by the quadratic relationship

$$\sigma = 8803.41 - 3.5228(T - T_m) + 9.8112 \times 10^{-4}(T - T_m)^2. \tag{1}$$

Most of the previous works were devoted to the investigation of the alloys in the liquid state well above the liquidus or to solidification processes [12,13]. At the same time, much less investigations are dedicated to the melting.

In the present paper, special attention was focused on the melting–solidification peculiarities of the lead–bismuth alloys. For that purpose, the electrical conductivity was measured for the $Pb_{40}Bi_{60}$, $Pb_{50}Bi_{50}$, eutectic $Pb_{44}Bi_{56}$ and near eutectic $Pb_{43}Bi_{57}$, $Pb_{45}Bi_{55}$, $Pb_{46}Bi_{54}$ alloys.

2. Experimental details

The electrical conductivity was measured by a contact method in accordance with the 4-point scheme. The

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[*] Corresponding author. Tel.: +38 032 2394270.
E-mail address: plevachuk@mail.lviv.ua (Yu. Plevachuk).

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experiments were performed in an argon atmosphere. BN-ceramic measuring cells in form of vertical cylindrical containers with the operating cavity height of 50 mm and 2.5 mm in diameter were used. Graphite electrodes for current and potential measurements were placed in the wall of the cell along its vertical axis. The potential electrodes were provided with WRe-5/20 thermocouples connected with graphite electrodes in close contact with the melt, for temperature measurements. The uncertainty of temperature determination was about 1 K at the melting–solidification region and increased to 1.5 K at 500 K. Single thermoelectrodes of these thermocouples were used for electrical conductivity determination. A homogeneous temperature field with deviations of upto 0.3 K in the range of absolute values up to 600 K has been created inside a furnace. Some negligible thermal expansion of the BN had no influence on the data. The metals employed had a purity of 99.999%. The components were melted and evacuated in sealed quartz ampoules at 10–15 Pa. The melt was heated to a temperature 150 K above the liquidus and maintained for about 1 h until the resistivity values between the intermediate potential electrodes coincided, indicating melt homogeneity. For further details of this method and its experimental realization we refer to [14].

The sample composition was accurate within 0.02 wt%. The measurements were carried out during monotonic heating and cooling cycles with a rate of 20 K/h. The resultant error of the electrical conductivity measurements is about 2%.

3. Results and discussion

The electrical conductivity results of the $Pb_{40}Bi_{60}$, $Pb_{50}Bi_{50}$, $Pb_{44}Bi_{56}$, $Pb_{43}Bi_{57}$, $Pb_{45}Bi_{55}$, and $Pb_{46}Bi_{54}$ alloys are presented in Figs. 1–3. As seen from Fig. 1(a) the $\sigma(T)$ curves for the $Pb_{40}Bi_{60}$ revealed a hysteresis during the melting and solidification in the temperature range of about 40 K. It was observed that the thermocycling increased the temperatures of the melting completion and the solidification start for some dozens of degrees compared to the liquidus indicated at the phase diagram [15]. After melting at about 402 K the electrical conductivity increases. It is suggested that a kink at the middle of the increasing function $\sigma(T)$, indicating an increase of the temperature coefficient of conductivity $d\sigma/dT$, is connected with reaching of the critical concentration of the metallic phase. Reaching the molten state the conductivity decreases gradually upon heating. At cooling down the decrease of the electrical conductivity starts at 444 K and complete at about 404 K.

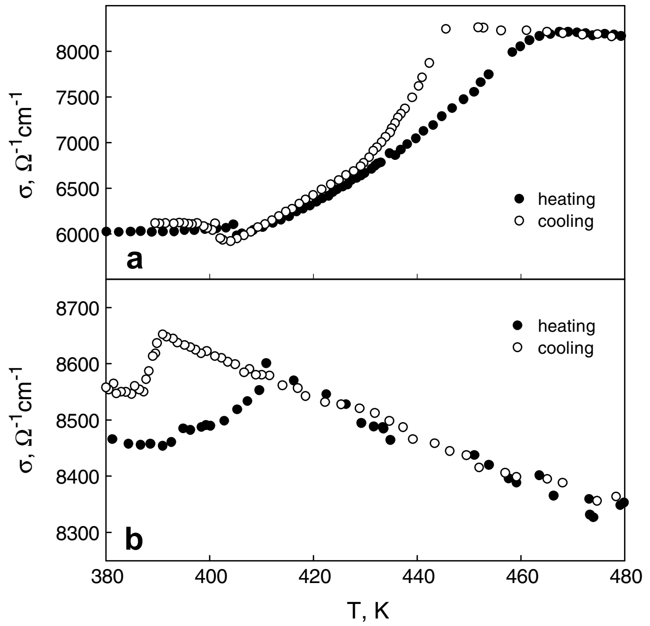

Fig. 1. Electrical conductivity vs. temperature for the (a) $Pb_{40}Bi_{60}$ and (b) $Pb_{43}Bi_{57}$ liquid alloys.

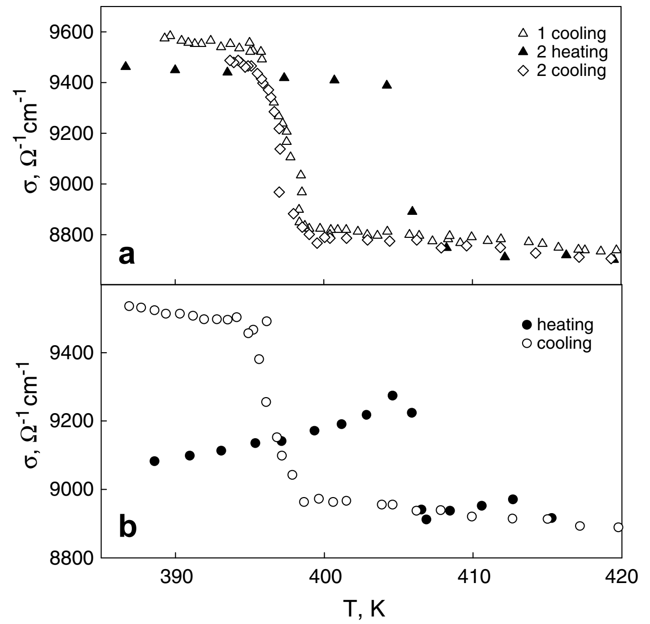

Fig. 2. Electrical conductivity vs. temperature for the (a) $Pb_{44}Bi_{56}$ and (b) $Pb_{45}Bi_{55}$ liquid alloys.

A similar conductivity behavior was revealed in the $Pb_{43}Bi_{57}$ liquid alloy (Fig. 1(b)). The eutectic composition $Pb_{44}Bi_{56}$ revealed a behavior similar to pure Pb (Fig. 2(a)). The electrical conductivity decreases with increasing temperature, falls drastically at the melting temperature, T_m, then decreases linearly with increasing temperature. Nevertheless, an influence of thermocycling is noticeable, and each following heating shifts the melting temperature to higher values. Solidification starts at the eutectic temperature and its range does not exceed several Kelvin. Additional studies were carried out for the melts $Pb_{45}Bi_{55}$ (Fig. 2(b)), and $Pb_{46}Bi_{54}$ (Fig. 3(a)), the compositions of which are very close to the eutectic one. The electrical conductivity of the $Pb_{45}Bi_{55}$ melt is very similar to that of the $Pb_{44}Bi_{56}$, while the $Pb_{46}Bi_{54}$ melt revealed a small temperature 'melting–solidification' hysteresis of about 12 K. The similar temperature dependence of the

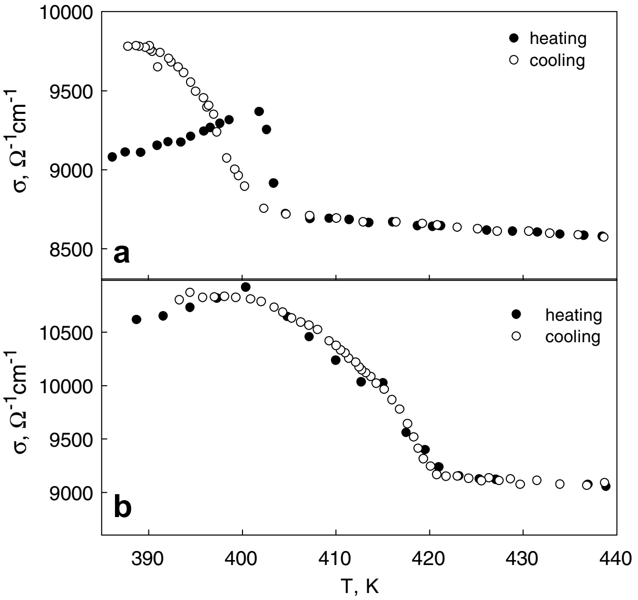

Fig. 3. Electrical conductivity vs. temperature for the (a) $Pb_{46}Bi_{54}$ and (b) $Pb_{50}Bi_{50}$ liquid alloys.

electrical conductivity suggests that the solidification processes in both the eutectic and near eutectic liquid alloys are almost identical. As seen from Fig. 3(b), the liquidus and solidus temperatures of the hypereutectic $Pb_{50}Bi_{50}$ liquid alloy were not sensitive to thermocycling and were the same during melting and solidification. The $\sigma(T)$ behavior for this composition is similar to that of pure Pb.

As mentioned in [11], the equilibrium of the solidification could be reached only upon a very slow cooling (20 K/h in our case). A restricted diffusion mass transfer leads to a non-equilibrium solidification, and the resulting solid solution is non-uniform in composition. That is why, different ways of eutectic transformations depending on the initial alloy composition are possible [16]. The first precipitated particles of the solid phase can be the crystallization nuclei for another phase. In this case the eutectic transformation occurs at the eutectic temperature, T_E. Otherwise, these particles are not the nuclei for another phase, but continue to precipitate with cooling below the T_E. Thus, the eutectic transformation occurs below the eutectic temperature. The range of undercooling also depends on the solidification rate. The studies revealed that the first precipitation particles are not necessarily nuclei for the development of the second phase in the Pb–Bi melts. The analysis of each composition as well as of the individual $\sigma(T)$ results displays that the eutectic transformation for $Pb_{44}Bi_{56}$ occurs at T_E. The undercooling of the compositions shifted oppositely with respect to the eutectic one occurs at different temperatures. The eutectic transformation of the melt enriched by Pb occurs at about 5 K below T_E and is similar to that of the eutectic $Pb_{44}Bi_{56}$, while the transformation of the melt enriched by Bi occurs at 2–3 K below T_E. It is suggested that the points of the jump-like $d\sigma/dT$ change can be considered as some specific points of the critical nucleation.

4. Conclusion

The investigations revealed some anomalies in the temperature dependence of electrical conductivity, such as hysteresis and heating–cooling curve divergence. An influence of thermocycling is noticeable for some alloys, and each following cycle shifts the melting point to higher values. The undercooling of the melts with compositions shifted oppositely with respect to the eutectic one occurs at different temperatures.

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