Melting-solidification process in Pb-Bi melts

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Abstract. Electrical conductivity, $\sigma(T)$, of liquid 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. A solidification mechanism is proposed.

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]. Therefore, it is of major practical interest to investigate the thermophysical properties of eutectic and near-eutectic Pb-Bi alloys. The Pb-Bi system has been studied repeatedly in the liquid state, nevertheless, the electrophysical data still remain scarce [2, 3]. Different compositions covering the concentration range between pure Pb and Bi were investigated (see [3] and references therein) but no special attention was focused on the melting-solidification peculiarities of the eutectic region in this system.

Although numerous studies are dedicated to solidification processes in one- and multi-component metal systems [4, 5], much less investigations are devoted to the melting peculiarities in metallic alloys. It is known that the liquidus, L, and solidus, S, lines determine a thermodynamic equilibrium between the coexisting liquid and solid phases with identical chemical potentials. Ideally, the equilibrium during solidification can only set in, when cooling of the melt is infinitely slow. In fact, a definite cooling rate as well as finite diffusion mass transfer suggests that a real equilibrium cannot be attained. Owing to this non-equilibrium solidification, the resulting solid solution is non-uniform in composition. The melting of metallic alloys is often considered as a process simply reversible to the solidification. Here a principal difference between melting of one- and multi-component systems must be emphasized. Melting of a one-component substance is connected with violation of crystalline lattice stability, while melting of an alloy consists in solving of the refractory fractions in the formed liquid. Melting and solidification can be considered as the reversible processes only when they occur in equilibrium.

The non-equilibrium solidification causes inevitably a deviation from the equilibrium leading, in turn, to an increase of the melting completion temperature. Thus, appearance of the refractory fractions as well as the gravitational liquation leads to an alloy overheating above the liquidus. Describing the alloys phase transformations one constructs often the lines of metastability running below the liquidus [6]. These lines correspond to the equilibrium between a liquid and a nucleus in
some concentration region and are located on the extension of the liquidus line below the eutectic point. Undercooling of metallic melts at zero temperature gradients is described not sufficiently well, besides the fact that certain specific points below the eutectic one are also not confirmed. One of the goals of this work is a complementation of the Pb-Bi phase diagram by some specific points. Temperature dependence of electrical conductivity was measured for this purpose.

2. Experimental details
The measurements of the electrical conductivity, \( \sigma(T) \), were carried out by a contact method in accordance with the 4-point scheme. The experiments were performed under argon gas pressure up to 10 MPa to minimize the change in the chemical composition. Measuring cells manufactured of BN ceramic in the form of vertical cylindrical containers with an operating cavity height of 60–mm were used. Graphite electrodes for current and potential measurements were placed in the wall of the container along its vertical axis. The potential electrodes were provided with thermocouples. These thermocouples were used for temperature measurements and their single thermoelectrodes for electrical conductivity and thermoelectric power measurements, respectively. The melt temperature was determined by WRe-5/20 thermocouples in close contact with the liquid. This method as well as the experimental equipment was described earlier in [7]. Pure Pb and Bi were melted and evacuated in sealed quartz ampoules at 10-15 Pa. Then each sample was inserted into the cell directly inside a high-pressure vessel. Thus, the sample composition was accurate within 0.02 wt.%. The resultant error of the electrical conductivity measurements is about 2%.

3. Results
Temperature dependence of the electrical conductivity of Pb_{40}Bi_{60}, Pb_{43}Bi_{57}, Pb_{44}Bi_{56}, Pb_{45}Bi_{55}, Pb_{46}Bi_{54}, and Pb_{50}Bi_{50} (at.%) liquid alloys was studied. The measured values are presented in Figures 1-3.

![Figure 1. Electrical conductivity vs. temperature for the Pb_{40}Bi_{60} (a) and Pb_{43}Bi_{57} (b) liquid alloys](image1)

![Figure 2. Electrical conductivity vs. temperature for the Pb_{44}Bi_{56} (a) and Pb_{45}Bi_{55} (b) liquid alloys](image2)
As seen from Figure 1a, the $\sigma(T)$ curves for Pb$40$Bi$60$ revealed a hysteresis during the melting and solidification processes. A solidification range extends from 444 K to 411 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 [8]. Figure 1 presents the results of a third melting-solidification cycle. A first small jump on the $\sigma(T)$ curves has been observed at 402 K during melting (solidus line). A next kink at about 432 K assuming an increase of the temperature coefficient of conductivity $d\sigma/dT$ is probably connected with reaching of the critical concentration of the crystalline phase. The melting ends at about 464 K that is reflected by further gradual decreasing of the electrical conductivity upon heating. Similar conductivity behavior has been revealed in the Pb$39$Bi$61$ liquid alloy (Figure 1b).

The eutectic composition Pb$44$Bi$56$ revealed a similar behavior compared to pure Pb (Figure 2a). 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 $T_m$ to higher values (up to 5 K). Solidification starts at the eutectic temperature and its range does not exceed 4-5 K.

Additional studies were carried out for the melts Pb$45$Bi$55$ (Figure 2b), and Pb$46$Bi$54$ (Figure 3a), the compositions of which are very close to the eutectic one. The electrical conductivity behavior of the Pb$45$Bi$55$ melt is very similar to that of the Pb$44$Bi$56$. The Pb$46$Bi$54$ melt revealed a small temperature “melting-solidification” hysteresis, i.e., solidification begins at ~ 402 K and comes to the end at 390 K. Similar temperature dependence of the electrical conductivity suggests that solidification processes in both the eutectic and near eutectic (within 1-2 at.%) liquid alloys are almost identical.

As seen from Figure 3b, the liquidus (423 K) and solidus (400 K) temperatures of the hypereutectic Pb$50$Bi$50$ liquid alloy did not depend on thermocycling and were the same during melting and solidification. A jump of the $d\sigma/dT$ was observed at 413 K. Generally, the $\sigma(T)$ behavior for this composition is similar to that for pure Pb.
4. Discussion
The investigations allow a phase diagram supplementation in the eutectic region with regard to the metastable region (see Figure 4). In addition to the liquidus lines L1 and L2, the lines of the “metastable” liquidus M1 and M2 are also presented. The latter are constructed from the experimental $\sigma(T)$ data. There are 4 intersections of the curves L1, L2, M1, and M2: the eutectic point E (between L1 and L2), point P1 (between L1 and M2), point P2 (between L2 and M1), and point P3 (between M1 and M2). We consider the ways of eutectic transformations depending on the initial alloy composition. Solidification of the melt composition X1 (e.g. Pb$_{50}$Bi$_{50}$), which is accompanied by an undercooling determined by M2, leads to precipitation of the solid Pb-Bi alloy. Its composition is determined by the solidus line. The liquid composition changes along L2 with decreasing temperature reaching the eutectic temperature E.

As shown in [6], two further processes are possible:

1) The first precipitated particles of the solid phase become the crystallization nuclei for another phase. In this case the eutectic transformation occurs at the eutectic point E.

2) These first precipitated particles do not become the crystallization nuclei for another phase, and the melt is not sensible to them. The particles continue to precipitate with decreasing temperature below the point E, and the liquid composition changes along the L2 extension. Reaching a temperature determined by the intersection of the curves L2 and M1 (P2), nuclei of the second phase (Bi) appear, and the eutectic transformation occurs in P2.

Solidification of the alloy with a composition X2 on another side of the eutectic composition (e.g. Pb$_{40}$Bi$_{60}$) proceeds similarly. The eutectic transformation will occur either in the points E or P1, depending on the influence of the first precipitates on the second liquid phase.

The eutectic transformation in the melt with a composition corresponding to point P3 takes place without initial nucleation, and its undercooling is a minimum relative to E.

Consider now a melt solidification of a composition between the points P3 and P4. After primary nuclei arise of a solid solution at a certain undercooling, determined by the line M2, the composition of the liquid changes with time at constant temperature towards an increase of the content of the second component. As soon as the content of the second phase reaches the line M1, the eutectic transformation occurs.

An increase of the solidification velocity leads to an enlargement of the undercooling region and to the M1 and M2 lines displacement. Respectively, positions of the points P1-P4 will also be shifted. In other words, the eutectic transformations can take place at rather shifted temperatures and concentrations.

The experimental results on the Pb$_{43}$Bi$_{57}$ melt provide further evidence to our suggestion about an existence of the metastable M-lines. This composition is located between the points E and P3 in the phase diagram. Taking into account that positions of the points E, P3 and P4 are determined with some errors as well as the fact that they are located very close to each other, the alloy Pb$_{43}$Bi$_{57}$ could lie between the points P4 and P3 or even between P3 and P2.

The solidification starts at about 391 K, and this temperature is found on the extension of the line M2, 7 K below the eutectic temperature. At the melt undercooling below the solidification temperature onset, the eutectic transformation starts as soon as the liquid composition reaches the line M1. The liquidus temperature during heating determined as 410 K, exceeds the L1 value. This is an evidence in favor of the metastable solidification leading to the refractory phases precipitation. Hence, the lines of liquidus and undercooling extend to the region below the eutectic melting temperature.

Our studies revealed that the first precipitation particles are not necessarily nuclei for the development of the second phase in the Pb-Bi melts. A precise analysis of each composition as well as of the individual $\sigma(T)$ results displays that the eutectic transformation coincides with the E point from the $\sigma(T)$ data. The undercooling of the melt compositions shifted oppositely with respect to the eutectic one occurs at different temperatures. The eutectic transformation of the melt enriched by Pb is found at about 5 K below E and is similar to that of the eutectic Pb$_{44}$Bi$_{56}$, while transformation of the melt enriched by Bi occurs at about 2 K below E (see Figure 4). It is suggested that the points of the
jump-like $\Delta\sigma/dT$ change can be considered as some specific points of the critical nucleation. Furthermore, a line of the critical nucleation can be constructed between the L and M lines. The latter requires, nevertheless, further investigations.

**Conclusion**

The studies filled a gap in the knowledge of electrophysical properties of the important binary Pb-Bi system. The investigations revealed the anomalies on the electrical conductivity vs. temperature curves, 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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