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STRUCTURE-SENSITIVE PROPERTIES OF MODEL HIGH-ENTROPY LIQUID ALLOYS

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Temperature dependence of electrical conductivity, σ(T), thermoelectric power, $S(T)$, and viscosity, $\eta(T)$, of model high-entropy liquid alloys were studied. Anomalous changes of thermophysical properties in the liquid binary $Pb_{26.1}Sn_{73.9}$, $Pb_{44}Bi_{56}$ and ternary $Bi_{46}Pb_{29}Sn_{25}$ eutectics have been revealed well above the liquidus. The temperature range of anomalies reaches hundreds degrees. The results are interpreted in the context of the assumption that the microsegregation areas exist in the eutectic systems.

Key words: Eutectic, Electrical conductivity, Thermoelectric power, Viscosity, Segregation

1 Introduction

Usually the most conventional alloys are based on one principal element. Different kinds of alloying elements are added to the principal element to improve its properties, forming an alloy family based on the principal element. For example, steel is based on Fe, and aluminium alloys are based on Al. However, the number of elements in the periodic table is limited, thus the alloy families that can be developed are also limited. The new concept, first proposed in 1995, has been named a high-entropy alloy (HEA). HEAs are defined as alloys with five or more principal elements. Each principal element should have a concentration between 5 and 35 at.% maximizing the configurational entropy. Besides principal elements, HEAs can contain minor elements, each below 5 at.%.

However, investigation of such multicomponent HEAs is very complicated, and at this point, information about the properties of their two and three component subsystems, which can serve as some model systems, is very important. Recently viscosity of the low temperature high-entropy melts Cu–Sn–Pb–Bi–Ga and Cu–Bi–Sn–In–Pb has been reported [1,2]. It is suggested that behaviour of electrical properties could give additional information for studies of HEAs. In this paper we report investigations of liquid binary $Pb_{26.1}Sn_{73.9}$, $Pb_{44}Bi_{56}$, and ternary $Bi_{46}Pb_{29}Sn_{25}$ alloys.

Although these systems were extensively studied, the measurements of their eutectic region reveal anomalous temperature dependencies of some physical properties. It was shown that molten metallic alloys undergo a number of structural transformations from the initial microheterogeneous state just after melting up to the true solution state [3].

As shown in recent theoretical studies (see [4] and references therein), a regular solution becomes thermodynamically unstable approaching to the eutectic temperature T_e. Not discussing the reason of this phenomenon, the areas of stability and instability separated by spinodal and binodal lines have been determined. It has been shown theoretically that a maximum temperature of instability did not exceed $2T_e$. Crossing this temperature upon cooling the regular solution becomes metastable. Further transition to the irregular state is possible either by fluctuation processes or under external fields. Crossing the spinodal, subsequent temperature decreasing transforms a system into the labile for the regular solution area, where any essential structure changes are not possible.

The anomalies of the resistivity, internal friction or density temperature dependencies, such as hysteresis and heating-cooling curve divergence were observed in the different eutectic systems [3, 5–7]. One explanation is connected with the structure transition of local short-range orders, when the previous bonds are broken to form new bonds or a new more disordered high-temperature liquid [5]. We suggest that similar structure rearrangement should be accompanied by the gradual properties changes, like e.g. in liquid tellurium [8], where structure modifications are essential [9].

In this work we decided to combine the studies of electrophysical and structure sensitive properties of the lead-based eutectics in a wide temperature range above the liquidus. Binary Pb-Sn, Pb-Bi and ternary Pb-Bi-Sn systems were chosen for investigations.

2 Experimental details

2.1 Electrical conductivity and thermoelectric power measurements

The measurements of the electrical conductivity, σ(T), and the thermoelectric power, $S(T)$, have been carried out by a contact method in accordance with the 4-point scheme. The experiments were performed under argon gas pressures up to 10 MPa to minimize the change in the chemical composition. Graphite electrodes for current and potential measurements were placed in the wall of the vertical cylindrical BN-ceramic measuring cell 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. The melt temperature was determined by WRe-5/20 thermocouples in close contact with the liquid. Temperature gradients of 15-20 K along the cell were additionally controlled to within 0.1 K by a preliminary calibrated 5-point differential thermocouple. The cell construction permits to carry out the electrical conductivity and thermoelectric power measurements simultaneously in one run. This method as well as the experimental equipment was described earlier in [10].

Pure Pb and Bi were melted in evacuated and 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%, and 5% for the thermoelectric power determination.

2.2 Viscosity measurements

The measurements of the viscosity were carried out using a computer-controlled oscillating-cup viscosimeter. Using the modified Roscoe equation, the dynamic viscosity, $\eta(T)$, has been calculated from the corresponding logarithmic decrement and the period of oscillations. The experiments were performed in helium atmosphere under a negligible excess pressure of about 0.02-0.03 MPa. The sample compositions of about 30 g were accurate to 0.02 wt. %. Each sample has been weighed before and after the measurements, and no loss of mass has been observed. Cylindrical graphite crucibles with internal diameter of 14 mm were used. A homogeneous temperature field up to 0.3 K in the range of absolute values up to 800 K has been created inside the furnace. The temperature has been measured with the WRe5/20 thermocouple arranged just below the crucible. The viscosity data were obtained with an accuracy of about 3%.

3 Results

The binary liquid alloys of the eutectic compositions $Pb_{26.1}Sn_{73.9}$, $Pb_{44}Bi_{56}$, the ternary eutectic $Bi_{46}Pb_{29}Sn_{25}$ and the $Pb_{50}Bi_{50}$ liquid alloy (all at.%) were chosen for the studies.

3.1 Viscosity and a melt structure model

The temperature dependencies of viscosity for the liquid $Pb_{26.1}Sn_{73.9}$ and $Pb_{44}Bi_{56}$ eutectics are presented in Figs. 1 and 2. The viscosity decreases exponentially with increasing temperature. Similar to previous viscosity studies dedicated to these systems [11–14], no peculiarities and anomalies were revealed in all the temperature range, at first glance.

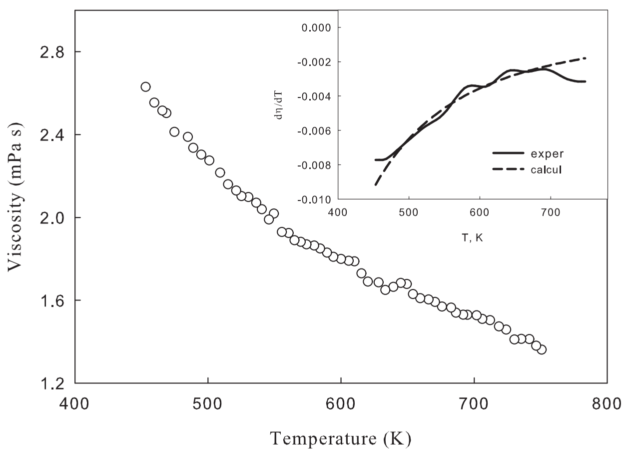

Рис. 1: Viscosity vs. temperature of the $Pb_{26.1}Sn_{73.9}$ liquid alloy.

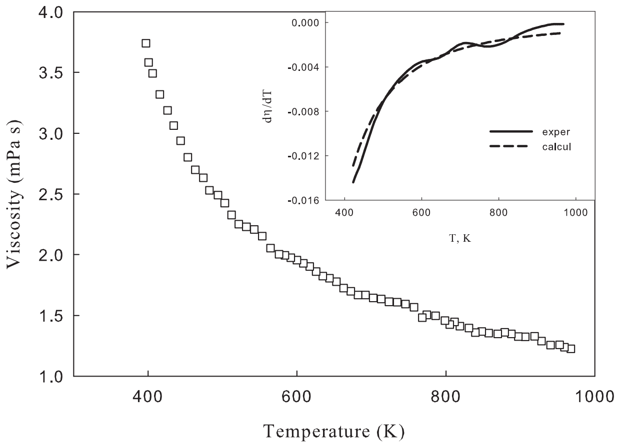

Рис. 2: Viscosity vs. temperature of the $Pb_{44}Bi_{56}$ liquid alloy.

However, the oscillations appear in the $d\eta/dT$ - temperature curve (insets of Figs. 1,2) specific for each melt temperature range. For comparison, the results of numerical differentiation of the Arrhenius equation $\eta = \eta_0 exp^{Q/RT}$ (η_0 is a constant, Q is the activation energy of viscous flow and R is the ideal gas constant) are also presented in Figs. 1,2. The parameters $\eta_0 = 0.6$ mPas and $Q = 5.915$ KJ/mol for $Pb_{44}Bi_{56}$ and $\eta_0 = 0.55$ mPas and $Q = 5.912$ KJ/mol for $Pb_{26.1}Sn_{73.9}$ are determined from the experimental dependence $\ln \eta = f(1/T)$. The oscillations observed are similar to those reported in [5] and suggest a metastable non-equilibrium quasieutectic structure, which keeps upon melting. According to Ref. [3] a similar structure after the melting can be considered as a microemultion or microsuspension of dispersed particles enriched in one of the components and surrounded by a molten matrix of another component. Owing to the difference in densities, a particle precipitation takes place. The full precipitation is counteracted by an intensive Brownian motion and leads, finally, to an inhomogeneous particle distribution with height.

3.2 Electrical conductivity and thermoelectric power

The electrical conductivity of all the melts investigated decreases with heating (Figs. 3-6). The data for the eutectic $Pb_{26.1}Sn_{73.9}$ are in good agreement with our previous results reported in [14] for a narrow temperature range after melting $T_m + (100 - 200K)$ and in [15].

Nevertheless, extending the temperature range and looking thoroughly into the electrical conductivity behavior, we observed some singularities on the $\sigma(T)$ dependencies, contrary to the expected smooth curves. These anomalies become more evident on the $\frac{d\sigma}{dT} = f(T)$ dependencies (see results in Figs. 3-6). The temperature range of significant $\frac{d\sigma}{dT}$ changes depends on the eutectic system as well as on the melt composition. This range extends from 600 to 1000 K for the $Pb_{26.1}Sn_{73.9}$ (Fig. 3), from 600 to 900

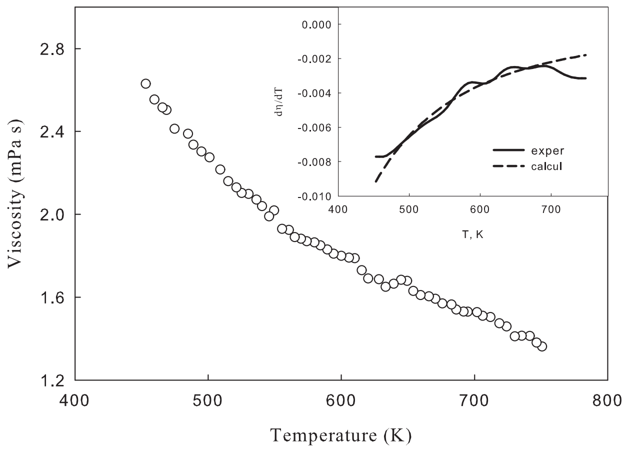

Рис. 3: Viscosity vs. temperature of the $Pb_{26.1}Sn_{73.9}$ liquid alloy.

K for the $Pb_{44}Bi_{56}$ (Fig. 4), from 550 to 950 K for the $Bi_{46}Pb_{29}Sn_{25}$ eutectic (Fig. 5) and from 550 to 1000 K for the near eutectic $Pb_{50}Bi_{50}$ melt (Fig. 6). It should be noted that an anomalous behavior of the thermoelectric power was also revealed (see Figs. 4,5). The thermoelectric power as a function of the carrier effective mass is more sensible to the structure changes in the system. Therefore, some discrepancy between the temperature ranges of anomaly behaviors revealed both on the $\sigma(T)$ and $S(T)$ curves is admissible, whereas the correlation between σ and S behaviors for each system is quite good. A hysteresis in the course of heating-cooling processes was observed for the $Pb_{26.1}Sn_{73.9}$ and also for $Pb_{50}Bi_{50}$ near-eutectic melts. In the later case the hysteresis is more pronounced.

The electrical conductivity of the $Pb_{50}Bi_{50}$ melt has been measured throughout the sample height. For this purpose a measuring cell was divided into two sections. A difference between $\sigma(T)$ values obtained during heating for the upper and lower sections in the temperature range from 750 to 1000 K also suggests the inhomogeneous particle distribution throughout the height (see Fig. 6). This difference vanished upon further heating and did not appear any more during cooling. All features mentioned above suggest a definite structure rearrangement in the eutectic systems. Note that these peculiarities for the $Pb-Bi$ system were not reported before [16].

4 Discussion

According to the model proposed in [4], areas of different thermodynamic stability in the liquid state exist in the eutectic systems. Similar to immiscible systems these areas are separated by spinodal and binodal lines. Nevertheless, no typical phase separation is observed here in an explicit form. These areas manifest themselves as anomalous fluctuations of concentration, reflected, in turn, as changes of the commonly predicted

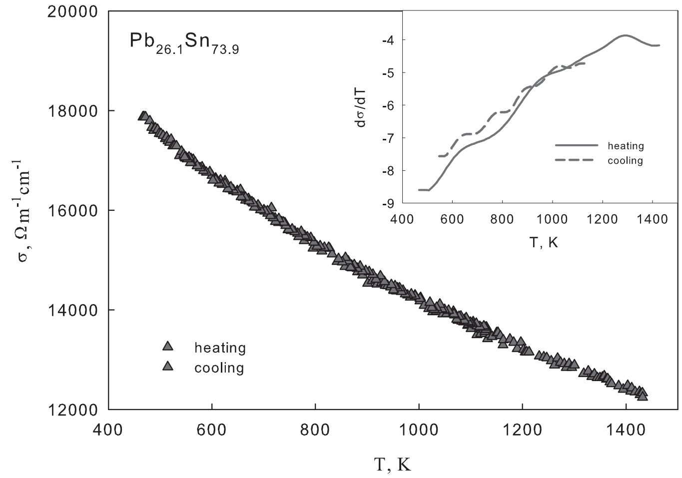

Рис. 4: Electrical conductivity vs. temperature of the $Pb_{26.1}Sn_{73.9}$ liquid alloy.

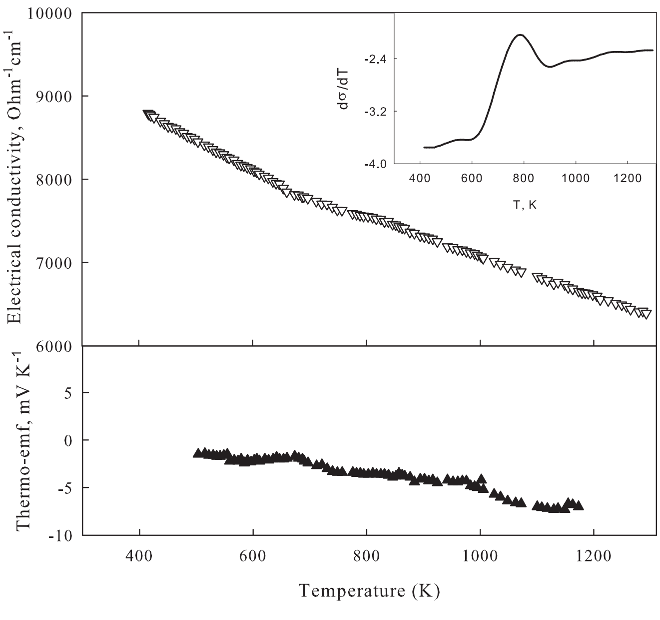

Рис. 5: Electrical conductivity and thermoelectric power vs. temperature of the $Pb_{44}Bi_{56}$ liquid alloy.

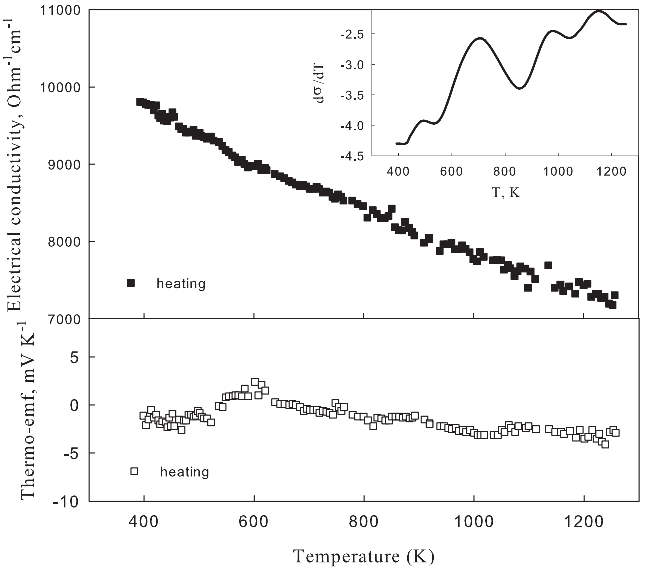

Рис. 6: Electrical conductivity and thermoelectric power vs. temperature of the $Bi_{46}Pb_{29}Sn_{25}$ liquid alloy.

physical properties. The observed phenomenon could be considered as a peculiar kind of micro segregation.

A quasi eutectic structure of the chemically heterogeneous melt remains after melting, and a concentration gradient is formed throughout the height. It is suggested that in the temperature range of the linear $\sigma(T)$ dependence (the slope of $\frac{d\sigma}{dT}$ is almost constant) reversible changes of composition and of the particle size occur. The particles are in the metastable equilibrium with a matrix. After reaching a specific for each composition temperature, reflected as a kink on the $\sigma(T)$ curve or a sharp $\frac{d\sigma}{dT}$ increase, the particle dissolution starts. The interfacial tension slows down the process, so that a microheterogeneous melt can remain even at rather high temperatures.

Determination of the limits of microheterogeneous stability in the eutectic melts by extrapolation of the limiting solubility curves in the solid state towards the overliquidus region has been proposed in Ref. [4]. This method was based on the ideas developed as earlier as in [17].

A spinodal as a border line of the homogeneous melt stability has a maximum, which cannot exceed $2T_E$. The results obtained in the present work do not confirm this statement. Missing of kinks on the $\sigma(T)$ curves and a weak temperature dependence of the $\frac{d\sigma}{dT}$ dependencies suggest higher characteristic values then $2T_E$ for each system.

The $2T_E$ value for the $Pb_{26.1}Sn_{73.9}$ eutectic is about 916 K; 796 K for the $Pb_{44}Bi_{56}$, and approx. 738 K for the $Bi_{46}Pb_{29}Sn_{25}$, while according to our experimental data, transition temperatures to the stable state are 1350 K for $Pb_{26.1}Sn_{73.9}$, 900 K for $Pb_{44}Bi_{56}$, and approx. 1150 K for the $Bi_{46}Pb_{29}Sn_{25}$.

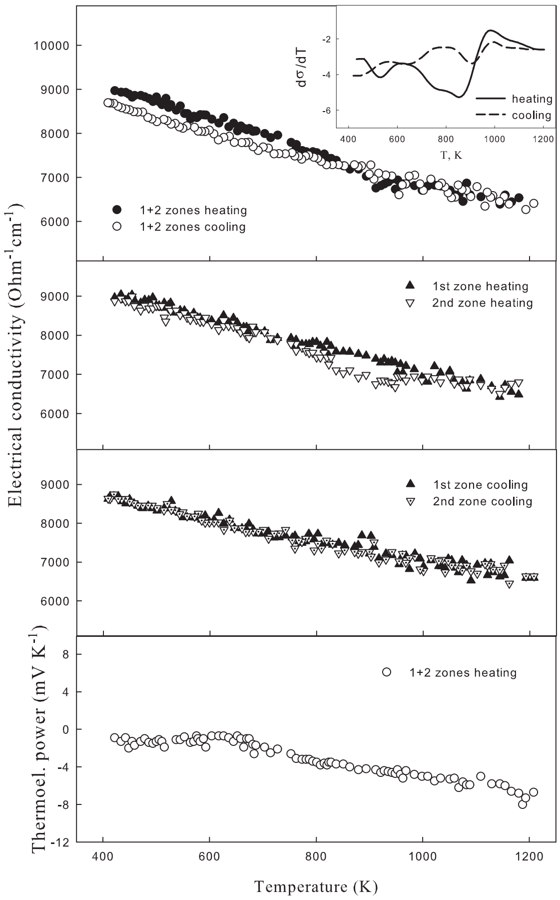

Рис. 7: Electrical conductivity and thermoelectric power vs. temperature of the $Pb_{50}Bi_{50}$ liquid alloy.

In other words, the binodal line constrains the area not of the unstable, but of the metastable quasieutectic melt structure. This line exceeds considerably the curves of the limiting solubility extrapolated towards the liquid phase. It is conceivable that the lower points of the binodal will coincide with the points of intersection of these curves and the eutectic horizontal. In actual practice, very rapid crossing of the temperature range between the limiting solubility curve and the liquidus prevents homogenizing of the solid phase. As a result, the heterogeneities will keep in the melt. Further heating leads to the approachment of the particle and surrounding melt compositions. At the upper point of the binodal these compositions coincide and the metastable state of the microemulsion further should not be possible. Nevertheless, we suggest that this metastable state can remain over a long period of time under the non-equilibrium conditions also at higher temperatures.

5 Conclusion

The revealed anomalies of electrophysical and structure properties in the eutectic melts confirmed an existence of different thermodynamic stability areas in the liquid state. The influence of heat treatment of the molten metallic alloy on the structure and properties of a final material within the specific working temperature range becomes significant in this connection. The results obtained will be valuable for understanding the properties of multicomponent high-entropy alloys in the wide temperature range of the liquid state.

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СТРУКТУРНО-ЧУТЛИВІ ВЛАСТИВОСТІ МОДЕЛЬНИХ ВИСОКОЕНТРОПІЙНИХ СПЛАВІВ

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Досліджено температурну залежність електропровідності, σ(T), термоЕРС, $S(T)$, та в'язкості, $\eta(T)$, модельних високоентропійних сплавів. Аномальні зміни теплофізичних властивостей подвійних $Pb_{26.1}Sn_{73.9}$, $Pb_{44}Bi_{56}$ та потрійних $Bi_{46}Pb_{29}Sn_{25}$ евтектичних розплавів було виявлено значно вище від иемпературы ліквідусу. Температурний діапазон аномалій становив сотні градусів. Результати проінтерпретовано в контексті припущення про існування мікророзшарування в евтектичних системах.

Ключові слова: Евтектика, Електропровідність, ТермоЕРС, В'язкість, Розшарування

СТРУКТУРНО-ЧУВСТВИТЕЛЬНЫЕ СВОЙСТВА МОДЕЛЬНЫХ ВЫСОКОЭНТРОПИЙНЫХ СПЛАВОВ

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Исследовано температурную зависимость єлектропровєдности, σ(T), термоЄДС, $S(T)$, и вязкости, $\eta(T)$, модельных высокоэнтропийных сплавов. Аномальные изменения теплофизических свойств двойных $Pb_{26.1}Sn_{73.9}$, $Pb_{44}Bi_{56}$ и тройных $Bi_{46}Pb_{29}Sn_{25}$ эевтектических разплавов виявлено значительно выше температури ликвидуса. Температурный диапазон аномалий составляет сотни градусов. Результаты проинтерпретировано в контексте предположения о существовании микрорасслоения в эвтектических системах.

Ключевые слова: Эвтектика, Электропроводность, ТермоЭДС, Вязкость, Расслоение