Thermal conductivity of rubidium–bismuth alloy of equiatomic composition

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Abstract. Experimental data on the thermal conductivity and thermal diffusivity of a liquid alloy RbBi of the equiatomic composition in the temperature range from the liquidus line to 1174 K have been obtained. The measurements were carried out on the basis of the laser flash method using a sealed steel cell. For studied properties the approximation equations and a table of recommended values are presented. The analysis of the obtained results confirms the existing assumption about liquid rubidium-bismuth alloys as associated solutions.

1. Introduction
Liquid alloys of alkali metals with bismuth belong to systems, in which in addition to the metallic type of chemical bond the ionic bond is manifested in varying degrees. The concentration dependences of the thermodynamic properties of these liquid systems (molar volume, thermal expansion coefficients, mixing entropy, Gibbs free energy of mixing) demonstrate strong deviations from the laws of ideal solution in the region of 25–50 at. % of Bi [1–3]. In the same region of compositions either sharp peaks or broad maximums are observed in the concentration dependence of the electrical resistivity [3]. According to modern concepts these effects are due to the existence of associated ionic complexes in the melt [3–6]. The concentration of these complexes reaches a maximum with certain stoichiometric compositions. Similar anomalies were found on the concentration dependences of the properties of liquid alloys of alkali metals with tin, indium and lead [4]. The theory of this phenomenon (sometimes called the “metal-nonmetal concentration transition”) is currently not fully developed. This is primarily due to the lack of detailed and reliable experimental data on many structurally sensitive properties and in particular transport properties of liquid alloys, in which the ionic nature of the interatomic interaction is manifested. According to the literature analysis the thermal conductivity coefficient of liquid Rb-Bi alloys hitherto has not been measured.

The purpose of this work was to study experimentally the coefficients of thermal conductivity (λ) and thermal diffusivity (α) of the RbBi alloy with equiatomic composition in a wide temperature range of the liquid state.

2. Experimental technique
The thermal conductivity coefficient of the liquid rubidium-bismuth alloy (50 at. % Bi) was studied by the laser flash method. The experimental setup and measurement technique are described in [7, 8] in detail. A measuring cell of 12Kh18N10T stainless steel of special geometry was used, in which a liquid sample was “clamped” between the crucible and lid, forming a flat layer of 2.6 mm thickness.
Rubidium and bismuth used for the preparation of the alloy had a purity of 99.94 and 99.98 wt. %, respectively. The alloy preparation was carried out in a glovebox filled with pure argon (99.992% by volume). The surfaces of metal ingots were preliminarily mechanically cleared from oxide films and nitrides. The weights of Rb and Bi pieces needed to calculate the equiatomic composition were determined on an analytical balance with an accuracy of 2–3 mg, taking into account “the effect of chemical contraction” [9] between these metals. The mass of the composite sample in the cell was 4.4 g. The actual Bi content in the studied alloy was 49.99 ± 0.02 at. %. The cell was sealed by arc welding directly in the inert atmosphere of the glovebox.

Before the experiments the cell was installed in a setup furnace, which was then evacuated and filled with argon up to 0.1 MPa pressure. The sample at the maximum temperature of the experiment was kept in the liquid state for some time for homogenizing. It should be noted that the small mass of the sample in the cell and the chemical reaction between liquid bismuth and rubidium [9, 10] ensured the homogeneity of the alloy in composition. The measurements were carried out in the cooling regime from a temperature of 1174 K to a solid state. The reproducibility of results in different thermal cycles confirmed chemical inertness of stainless steel to the liquid RbBi alloy.

The processing of primary data was carried out on a three-layer model (crucible – melt – lid) based on the developed software package [7, 8]. The two-dimensional heat equation was solved in cylindrical coordinates. When processing the properties of the cell material, as well as the density (ρ) and heat capacity (c_p) of the alloy were assumed to be known. Fitting parameters for the calculation were the thermal conductivity of the melt and emissivity of the external surfaces of the cell. The emissivity was actually an effective value responsible for all heat loss of the cell, including conductive and convective heat transfer in the surrounding gas medium. The data on ρ and c_p of the studied alloy were obtained before by the gamma-ray attenuation technique [10] and isoperibol drop calorimetry [11] with an accuracy of 0.4 and 1.5%, respectively. The change in the melt layer thickness was taken into account through the thermal expansion of the cell material. The error in measuring the thermal conductivity of a liquid alloy was 4–6% depending on the temperature. The magnitude of this error was mainly due to the uncertainty of the cell material properties, as well as the error of heat capacity of the studied alloy [7, 8].

3. Results and discussion

The measurement results of thermal conductivity λ of liquid RbBi alloy in the temperature interval 610–1174 K are presented in figure 1. The graph also contains data on the thermal conductivity of fluoride molten salt FLiNaK [12] and the values of λ_{add} calculated according to the additivity rule (λ_{add} = 0.5λ_{Rb} + 0.5λ_{Bi}). Data for λ_{Rb} and λ_{Bi} were taken from [8, 13]. Thermal conductivity of high temperature FLiNaK was determined also by the laser flash technique. For measurements in [12] a special designed graphite crucible was used. As can be seen from figure 1, RbBi alloy has the low thermal conductivity values typical of liquid salts [12] and its λ is an order of magnitude smaller than the value of λ_{add}, which confirms the existing assumptions [3–6] about intermetallic complexes in alkali metal-bismuth type liquid alloys.

The approximation of the obtained results from the temperature by the least squares method has given the following equation:

\[
λ(T) = -0.586 + 0.0034 T - 5.868 \times 10^{-7} T^2,
\]

where λ is in W/(m K), T is in K. The standard deviation of the experimental points from (1) does not exceed 1.4%.

According to the measurement results of λ and the literature data for ρ and c_p, the thermal diffusivity coefficient (a) of the alloy was calculated by the formula:

\[
a = \frac{λ}{ρ \cdot c_p}.
\]
The approximation equation for $a$ in the same temperature range as for $\lambda$ has the form:

$$a(T) = -0.325 + 1.87 \times 10^{-3} T + 2.734 \times 10^{-7} T^2,$$

(3)

where $a$ is in mm$^2$/s. The standard deviation of the calculated points from (3) does not exceed 1.3%. The error in determining $a$ by formula (2) coincides practically with the error of $\lambda$, since they differ in a known multiplier $\rho c_p$. The data of $\rho$ and $c_p$ have been used in determining $\lambda$, therefore their uncertainties already are included in the overall error of $\lambda$.

![Figure 1. The thermal conductivity of the liquid alloy RbBi (50 at. % Bi). 1 – our experimental data, 2 – equation (1), 3 – $\lambda$ data of the fluoride molten salt FLiNaK [12], 4 – $\lambda_{add}$.](image)

Table 1 shows the smoothed values of $\lambda$ and $a$ with their errors.

| $T$, K | $\lambda$, W/(m K) | $a$, mm$^2$/s | $\delta\lambda$, $\delta a$, % |
|-------|-------------------|--------------|------------------------|
| 610   | 1.27              | 0.92         | 4                      |
| 700   | 1.51              | 1.12         | 4                      |
| 800   | 1.76              | 1.35         | 5                      |
| 900   | 2.00              | 1.58         | 5                      |
| 1000  | 2.23              | 1.82         | 5                      |
| 1100  | 2.44              | 2.06         | 6                      |
| 1174  | 2.60              | 2.25         | 6                      |
Conclusion
The thermal conductivity of alkali metal-bismuth type alloy was measured for the first time. New experimental data on $\lambda$ and $a$ for liquid RbBi of the equiatomic composition in the temperature range from the liquidus line to 1174 K with an error of 4–6% have been obtained. It is shown that the alloy has low $\lambda$ values typical of molten salts and its $\lambda$ is an order of magnitude smaller than the thermal conductivity calculated according to the additivity rule.

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