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Experimental Investigations of Phase Equilibria in Binary Liquid Immiscible Alloys[1]

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Electroconductivity measurements for liquid metal (Tl, In)–chalcogen (Se, Te) alloys were performed in concentration range of their miscibility gaps. The experiments have been carried out under excess pressure of argon gas (up to 50 MPa) at temperatures up to 1200 K. Many-sectional measuring cell allows simultaneous determination of the electroconductivities of both separated liquids in entire range of the miscibility gap. The liquid–liquid coexistence curves for Tl–Se, Tl–Te, In–Se, and In–Te systems were constructed and critical point data were evaluated. The critical indices were also estimated. The results are analyzed in comparison to available data for fluid metals in vicinity of the liquid–vapor critical point.

KEY WORDS: binary alloys; critical point; electrical conductivity; high temperatures; liquid–liquid equilibrium; miscibility gap.

1. INTRODUCTION

Phase diagrams of some liquid binary alloys exhibit miscibility gaps in the temperature–concentration (T–x) plane [1]. In contrast to dielectric solutions, such mixtures are relatively less well studied. There is no information about the liquid–liquid coexistence curves and critical point data for many immiscible alloys. The situation arises due to the difficulties of high-temperature measurements and the absence of a generally accepted measuring technique and, subsequently, is caused by peculiarities of each experimental method employed. Furthermore, in the case of conductive fluids the role of

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electron subsystem in the critical point region and its possible influence on shaping of the phase equilibrium curve cannot be neglected [2, 3]. Therefore, experimental measurements of physical properties sensitive to the presence of conductivity electrons, for example, electroconductivity, seem to be suitable and promising for investigations of liquid–liquid equilibrium in binary immiscible alloys, especially those having a metal-to-nonmetal transition [4].

In this paper we summarize and report our experimental results on electroconductivity investigations of liquid–liquid equilibrium for liquid Tl–Se, Tl–Te, In–Se, and In–Te alloys. The shapes of the coexistence curves are analyzed in comparison to available data for other immiscible alloys and for fluid metals in the vicinity of the liquid–vapor critical point.

2. EXPERIMENTAL

The experiments were performed at temperatures up to 1200 K under excess pressure of argon gas (up to 50 MPa) to provide constant chemical composition of the samples. The electroconductivity measurements were carried out by a contact method in accordance with the four-point scheme. Original measuring cells used for this purpose were manufactured of boron nitride ceramic in the form of vertical cylindrical containers with an operating cavity height of 55 to 60 mm and a diameter of 1.8 to 3.5 mm. Seven graphite electrodes, two for current (at the top and the bottom) and five for potential measurements, were placed in the wall of the container along its vertical axis. An alternating current at 63 Hz was passed between the top and the bottom current electrodes through the liquid sample in the operating cavity. At the same time, voltage drops were measured for each of the vertical sections formed by the potential electrodes. Taking into account appropriate geometrical factors, electroconductivity $\sigma(T)$ values for each of the sections were then calculated based on measured current and voltage drops. The apparatus and the measurement procedure were all identical to those described in Ref. 5. Temperature gradients along the cell were controlled to within 0.1 K by a special five-point Pt/Pt–Rh differential thermocouple. The error of $\sigma(T)$ determination did not exceed 1.5%.

Accurately weighed (to within 10^{-4} g) amounts of constituent elements were melted in evacuated and sealed quartz ampoules at 10 Pa. Each of the samples was then filled into the cell in an inert argon gas atmosphere directly inside a high-pressure chamber. Thus, the initial chemical composition of the samples was accurate to within 0.02 at% during the complete run of the measurement. Each measuring cell was initially heated to a maximum temperature of approximately 1200 K and maintained carefully until the resistivities between the five intermediate potential electrodes coincided. The homogeneous alloy was then gradually cooled at a rate of 8 to 10 $K \cdot h^{-1}$ corresponding to quasi-equilibrium conditions.

3. RESULTS

As a typical example of the behavior of all the investigated systems, Fig. 1 shows the electroconductivity $\sigma(T)$ data for liquid Tl–Se alloys over the concentration range of the miscibility gap. The electroconductivity of completely mixed melts reveals a linear dependence with temperature. Moreover, the absolute values of $\sigma(T)$ in the high-temperature region above a consolute point are determined mainly by the sample concentration. Cooling the homogeneous alloys from 1200 K is accompanied by a negligible change in their electron properties. This behavior persists when temperatures are lowered until the phase separation point $T_S(x)$ is reached. The latter is determined for each alloy by its component concentration. Upon reaching the transition temperature $T_S(x)$, gravity separates the melt into two distinct phases, and a horizontal boundary surface between the liquid layers, the so-called meniscus, appears. Further cooling under natural conditions is accompanied by a continuous component redistribution. The

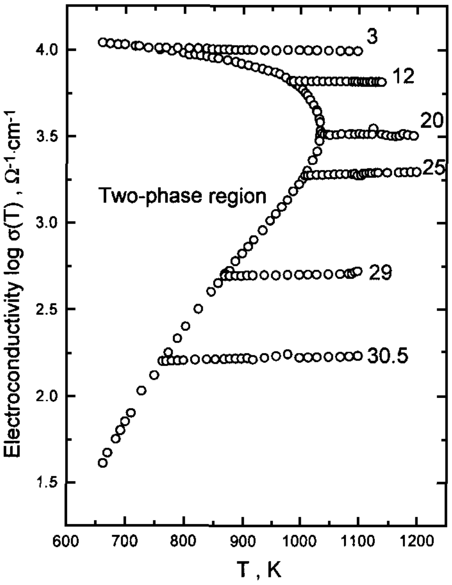

Fig. 1. Electroconductivity data log $\sigma(T)$ for Tl–Se liquid alloys; numbers denote the alloy concentration as at% Se.

denser liquid displaced below the meniscus is enriched by Tl (or In) at the expense of the less dense upper liquid. The latter, in turn, is enriched by Se (or Te). The concentrations of the coexisting phases x_1 and x_2 are simply determined by their temperature in correspondence to the liquid–liquid coexistence curve, which is the locus of $T_S(x)$ points on the binary system phase diagram.

For identical temperature reductions, different concentration changes for each phase form the different temperature dependences of electron properties of coexisting liquids. This manifested itself in our experiments as the beginning of a $\sigma(T)$ divergence at the $T_S(x)$ point. As an example of such typical behavior, Fig. 2 shows the results for a liquid $Tl_{85}Se_{15}$ alloy, that is, the conductivity versus temperature data for four different sections of the measuring cell. Sections 1 and 2 were Tl-rich, and their electroconductivities $\sigma_1(T)$ and $\sigma_2(T)$ were identical throughout the experiment. In turn, Section 4 was Se-rich, and its electroconductivity agreed with $\sigma_1(T)$ and $\sigma_2(T)$ only above the transition temperature, departing from them very drastically below $T_S(x)$. Section 3 was identical to the other sections only above this point; below $T_S(x)$, it showed a behavior intermediate between Section 4 and Sections 1 and 2. This behavior implies that Section 3

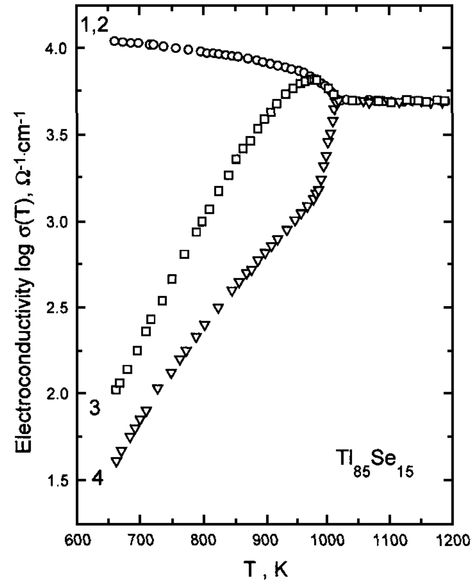

Fig. 2. Electroconductivity log $\sigma(T)$ for liquid $Tl_{85}Se_{15}$ alloy; 1–4, sections of the measuring cell numbered from the bottom.

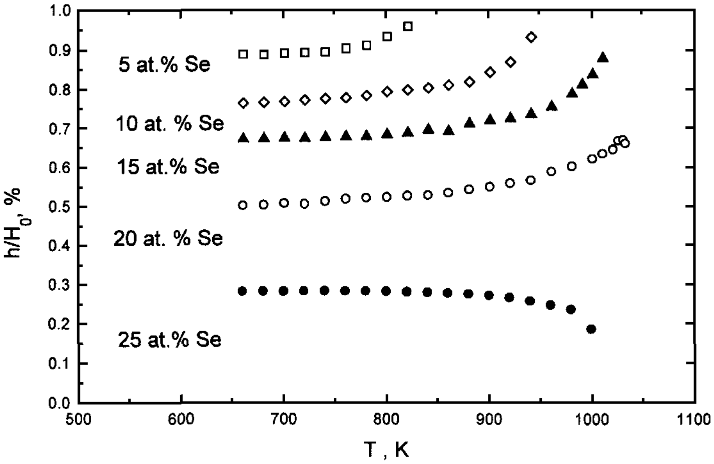

Fig. 3. Calculated position of the liquid–liquid interface as a function of temperature for Tl–Se alloys. h, height of the denser Tl-rich layer; H_0, total height of the melt column.

contained the meniscus almost over the entire temperature range of the two-phase coexistence. Moreover, considering the resistivity of this section and/or the resistivity along the entire height of the melt column as a resulting value of successively connected resistivities of the separated lower and upper liquid layers, it is possible to derive volume fractions of the coexisting phases.

The relation between these fractions and their variation with temperature are reflected as a vertical displacement of the meniscus. Results of such calculations, being typical for all the investigated binaries, are shown in Fig. 3. With regard to the $\sigma(T)$ absolute values, the difference between the properties of the coexisting liquids increases with cooling of the sample. At a temperature slightly higher than the monotectic line, the electroconductivities of the Tl-rich and the Se-rich layers differ almost by a factor of 300. Nevertheless, the low-temperature branches of diverging $\sigma(T)$ dependences for the alloys of various concentrations overlap. The full picture of the property changes of the separated phases over the entire miscibility gap is observed in a single experiment when a sample of critical composition x_C is studied. In this case the $\sigma(T)$ curve divergence takes place at the critical point T_C.

4. DISCUSSION

The phase separation $T_S(x)$ points determined after $\sigma(T)$ measurements for the alloys of different concentrations can be used to construct the

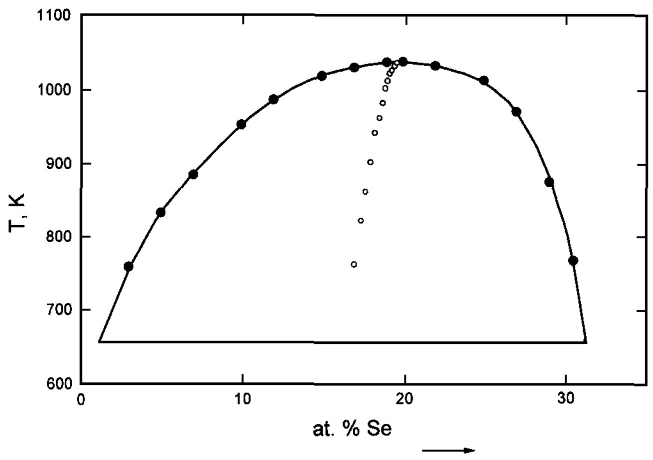

Fig. 4. Liquid–liquid coexistence curve of the Tl–Se system.

liquid–liquid coexistence curve and to estimate the critical point parameters in the phase diagram for each of the investigated binary systems. As an example, the equilibrium line of the Tl–Se system is shown in Fig. 4. The critical concentration and temperature were determined to be $x_C = 19.7 \pm 0.1$ at% Se and $T_C = 1036 \pm 2$ K. For more details, see Ref. 6. Our experimental data for the Tl–Se system are in good agreement with results of sound velocity investigations [7].

For the Tl–Te system, the critical temperature $T_C = 949 \pm 2$ K was determined at the critical concentration $x_C = 19.6 \pm 0.1$ at% Te [8]. The data agree with results obtained using a similar measuring technique in vacuum [9] and differ slightly from those obtained by DTA experiments [10] and drop-calorimetric measurements [11].

The critical point parameters for the liquid In–Se system were evaluated to be $x_C = 19.2 \pm 0.1$ at% Se and $T_C = 949 \pm 2$ K [12]. To our knowledge, the concentration range of miscibility gap has not been studied previously for this system.

For the electroconductivity measurements for liquid immiscible In–Te alloys, the values of critical temperature and concentration for this binary system were derived to be $T_C = 817 \pm 2$ K and $x_C = 19.8 \pm 0.1$ at% Te. Recently performed experiments on shear viscosity [13] have yielded critical point parameters of $T_C = 800 \pm 1$ K and $x_C = 18.6 \pm 1.3$ at%. The latter almost coincides with the data of ultrasonic investigations [14, 15] where the critical temperature $T_C = 802 \pm 3$ K, and two values of the critical concentration, namely, 18.35 at% Te and 19.2 at% Te, were reported. Earlier the critical temperature of 801 K at the critical concentration of 20 at% Te was reported for the In–Te system from measurements of maximal pressure in a gaseous bubble [16]. Presently, the latter together with data of Ref. 17, namely, $T_C = 806$ K and $x_C = 18$ at% Te, are given in Ref. 1 as reference values for the In–Te system. The observed discrepancy in absolute values of the critical parameters could be explained based on the peculiarities of each experimental technique used.

The liquid–liquid equilibrium lines for all the investigated binary systems are asymmetrical and their diameters, i.e., the locus of the tie-line midpoints $x_d = (x_1 + x_2)/2$, exhibit a nonlinearity near the liquid–liquid critical point (x_C, T_C) [6, 8, 12].

Studies of different fluid systems have revealed that corrections to asymptotic scaling must be applied when the range accessible to experiments exceeds the range of asymptotic validity of the scaling laws [18]. Thus, the expansions for the coexisting densities and/or concentrations, describing the shape of the equilibrium curve and its diameter, have the form

$$\frac{\Delta x}{x_C} = \frac{|x_1 - x_2|}{2x_C} = B_0 \varepsilon^{\beta} + B_1 \varepsilon^{\beta + \Delta_1} + \cdots \tag{1}$$

$$\frac{x_d}{x_C} = \frac{x_1 + x_2}{2x_C} = 1 + D_0 \varepsilon^{1-\alpha} + D_1 \varepsilon + D_2 \varepsilon^{1-\alpha+\Delta_1} + \cdots \tag{2}$$

where $\varepsilon = (T_C - T)/T_C$ is the reduced temperature, x_C is the critical concentration, x_1 and x_2 are the concentrations of coexisting phases, B_i and D_i are expansion coefficients, and β and α are critical indices. On the basis of Eqs. (1) and (2) with nonanalytic $(B_i = 0, D_i = 0, i = 1, 2, 3,\ldots)$ corrections being neglected, the analysis of the coexistence curve and the behavior of its diameter in the vicinity of T_C may be performed by the use of a single power law. The values of the critical indices β and α as well as preexponential factors B_0 and D_0 were estimated from the slopes of $\log\{(x_1 - x_2)/2x_C\}$ and $\log(x_d/x_C - 1)$ as a function of $\log \varepsilon$ [6, 8, 12]. It was found that the coexistence curves of the systems studied can be well described by an exponent $\beta = 0.34$ to 0.35 over the range $10^{-3} \leqslant \varepsilon \leqslant 10^{-2}$. These values of the β index agree with available data for fluid metals in the vicinity of the liquid–vapor critical point for which the parameter β lies between 0.35 and 0.36 [19]; similar results have been obtained for liquid immiscible metal binaries [9, 20–22]. The temperature behavior of the singular part in their diameters is well described by a simple power law with exponent $1 - \alpha$ varying between 0.86 and 0.88 [6, 8, 12], also similar to those of expanded Hg, Cs, and Rb [19, 23].

Since the index α characterizes a singular temperature dependence of the internal energy near a critical point, it was suggested [24] that the high amplitudes of the singularities in the coexistence curve diameter of Cs and Rb arise from the correspondingly strong thermodynamic state dependence of the screened ion–ion interactions in these fluids, especially as the metal-insulator transition is traversed. Our experiments give additional evidence in favor of this suggestion and allow the extension of the range of its applicability.

The coexistence curves were found to be asymmetric. According to Ref. 25, the asymmetry is expected for systems with strong concentration variation of the electronic screening which occurs as a precursor of the metal–nonmetal transition. In the case of liquid In–Te, In–Se, Tl–Te, and Tl–Se alloys, the miscibility gap occurs clearly more on the metallic side of the transition. An increase in the Se (or Te) content in these melts is accompanied by a partial localization of conduction electrons and is consequently demonstrated by the electroconductivity decreasing in a wide range of absolute values. This behavior shows also that the length of ion–ion interaction screening by the free-electron gas varies strongly with the alloy concentration.

5. CONCLUSIONS

The experimental technique for electroconductivity measurements in a wide temperature range is suitable for investigation of phase equilibria in binary liquid immiscible alloys. The many-sectional measuring cell allows simultaneous determination of the electroconductivities of both separated liquids over the concentration range of the miscibility gap. From such data, the shape of the liquid–liquid coexistence curve and the critical point parameters can be determined. The proposed method is also convenient for investigation of the meniscus behavior in opaque conducting immiscible liquids.

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