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The miscibility gap region and properties of liquid ternary alloys

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Abstract. Electrical conductivity measurements were performed for liquid immiscible $\text{Tl}_{0.80}(\text{Se}_x\text{Te}_{1-x})_{0.20}$ alloys in a wide temperature range under ambient pressures of argon gas (up to 50 MPa). The electrical conductivity shows the same behaviour as for binary liquid alloys during the mixing–demixing process. It was revealed that variation in the Se-to-Te ratio at a constant content of Tl changes the properties of coexisting liquids and affects the temperature of phase separation. The results are analysed in comparison with available data for binary immiscible Tl–Se and Tl–Te system alloys and the possible influence of the ion subsystem on the formation of the critical point parameters is discussed.

1. Introduction

A large number of liquid alloys exhibit a limited mutual component solubility, i.e. the binary phase diagrams show a miscibility gap which represents the equilibrium between two liquids of different compositions [1]. These systems have gained renewed interest as a result of material research in space. In the absence of a gravity field it should be possible to produce homogeneously dispersed alloys instead of a two-separated-layer structure as under the normal conditions on Earth. A great deal of effort has been devoted to understanding the nature of immiscible metal alloys during the last few years [2, 3]. These studies were mainly related to experimental investigations of different physical properties, as well as to thermodynamic calculations for the binary liquid alloys. As regards the ternary immiscible alloys, investigations of phase equilibria were reported recently for the Cd–Ga–Hg system [4].

In this paper we present experimental results of electrical conductivity measurements for the Tl–Se–Te immiscible alloys and report data concerning the region of liquid–liquid equilibrium, namely the dependence of the phase separation temperature on the Se-to-Te ratio at a constant concentration of Tl. Further, a possible influence of ion subsystem on the shaping of liquid–liquid critical point parameters is discussed briefly also.

2. Experimental details

Experiments were performed under ambient pressures of argon gas (up to 50 MPa) to provide a constant chemical composition of the samples. Electrical conductivity measurements have been carried out by a contact method in accordance with the four-point scheme. Original measuring cells, manufactured from boron nitride ceramic in the form of vertical containers

with an operating cavity height of 55 mm and a diameter of 3.5 mm, were used for this purpose. 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. The apparatus and the measurement procedure were identical with those described earlier in [5]. Temperature gradients along the cell were additionally controlled to within 0.1 K by a five-point Pt/Pt–Rh differential thermocouple. The error in the $\sigma(T)$ determination did not exceed 1.5%.

Accurately weighed (to within 10^{-4} g) amounts of Tl (99.99% metallic purity), Se (99.999%) and Te (99.999%) were melted in evacuated and sealed quartz ampoules at 10 Pa. Each of the samples was then placed into the cell directly inside a high-pressure vessel. Thus, the sample composition was accurate to within 0.02 at.%. 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 8–10 K h⁻¹ corresponding to quasi-equilibrium conditions.

3. Results

The electrical conductivity measurements were performed for ternary $\text{Tl}_{0.80}(\text{Se}_x\text{Te}_{1-x})_{0.20}$ alloys where $x = 0.90, 0.75, 0.60, 0.50, 0.40, 0.25$ and 0.10 . The electrical conductivity $\sigma(T)$ data for alloys with $x = 0.75, 0.50$ and 0.25 are shown in figures 1, 2 and 3, respectively. The same behaviour of electrical conductivity was observed also for other alloys investigated. As can be seen, cooling the completely mixed melts from 1200 K is accompanied by a negligible change in their electronic properties. Moreover, the absolute values of $\sigma(T)$ in the high-temperature region above a mixing point are determined mainly by the initial sample concentration. Upon reaching the phase separation temperature $T_S(x)$, gravity separates the melt into two distinct phases, and a horizontal boundary surface, the so-called meniscus, between the liquid layers appears. Further cooling under natural conditions is accompanied by a continuous component redistribution. The lower denser layer is enriched by Tl at the expense of the less dense upper liquid. The latter, in turn, is enriched by Se and Te. At identical temperature decreases, essentially different changes for each phase form the different temperature dependences of the electronic properties of coexisting liquids. This manifested itself in our experiments as the beginning of a $\sigma(T)$ divergence at the $T_S(x)$ point into the following two branches: $\sigma_L(T)$ describes the electrical conductivity of the lower liquid while $\sigma_U(T)$ describes the electrical conductivity of the upper liquid. In the case of binary alloys the full picture of the changes in properties of the separated phases over the entire temperature–concentration range of liquid–liquid coexistence is observed when a sample of the critical concentration x_C is studied and the $\sigma(T)$ curve divergence takes place at the binodal critical point T_C .

Our experimental results show that the electrical conductivity $\sigma_L(T)$ of the lower Tl-enriched phase in $\text{Tl}_{0.80}(\text{Se}_x\text{Te}_{1-x})_{0.20}$ alloys is almost insensitive to the substitution of Se by Te. For example, the electroconductivities $\sigma_L(T)$ at 800 K are almost the same for all these melts and equal to $10\,200\ \Omega^{-1}\ \text{cm}^{-1}$. However, the electrical conductivity $\sigma_U(T)$ of the upper liquid layer depends essentially on the Se-to-Te ratio. At the same temperature of 800 K, the electrical conductivity $\sigma_U(T)$ is equal to $360\ \Omega^{-1}\ \text{cm}^{-1}$ for the $\text{Tl}_{0.80}\text{Se}_{0.15}\text{Te}_{0.05}$ alloy and increases to values of $570\ \Omega^{-1}\ \text{cm}^{-1}$ and $910\ \Omega^{-1}\ \text{cm}^{-1}$ for the $\text{Tl}_{0.80}\text{Se}_{0.10}\text{Te}_{0.10}$ and $\text{Tl}_{0.80}\text{Se}_{0.05}\text{Te}_{0.15}$ melts, respectively. Furthermore, as can be seen from figures 1–3 the phase separation temperature $T_S(x)$ depends strongly on the Se-to-Te ratio. In comparison with the binary $\text{Tl}_{0.80}\text{Se}_{0.20}$ alloy ($T_S = 1035\ \text{K}$) the phase separation temperature of the

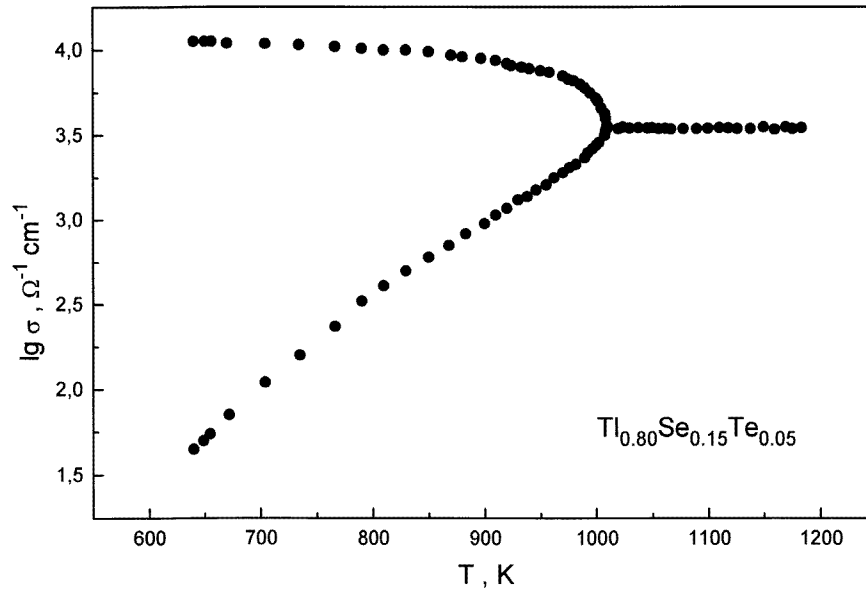


Figure 1. Temperature dependence of the electrical conductivity for the liquid $\text{Tl}_{0.80}\text{Se}_{0.15}\text{Te}_{0.05}$ alloy.

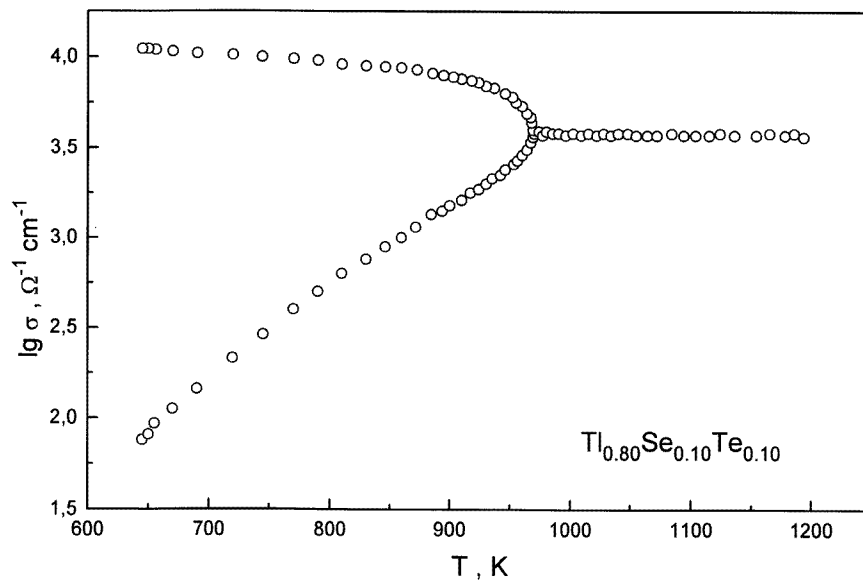


Figure 2. Temperature dependence of the electrical conductivity for the liquid $\text{Tl}_{0.80}\text{Se}_{0.10}\text{Te}_{0.10}$ alloy.

$\text{Tl}_{0.80}\text{Se}_{0.15}\text{Te}_{0.05}$ melt was determined to be equal to 1010 K and decreases further upon substitution of Se by Te to the values of 968 K and 920 K for the liquid $\text{Tl}_{0.80}\text{Se}_{0.10}\text{Te}_{0.10}$ and $\text{Tl}_{0.80}\text{Se}_{0.05}\text{Te}_{0.15}$ alloys, respectively. The dependence of the phase separation temperature

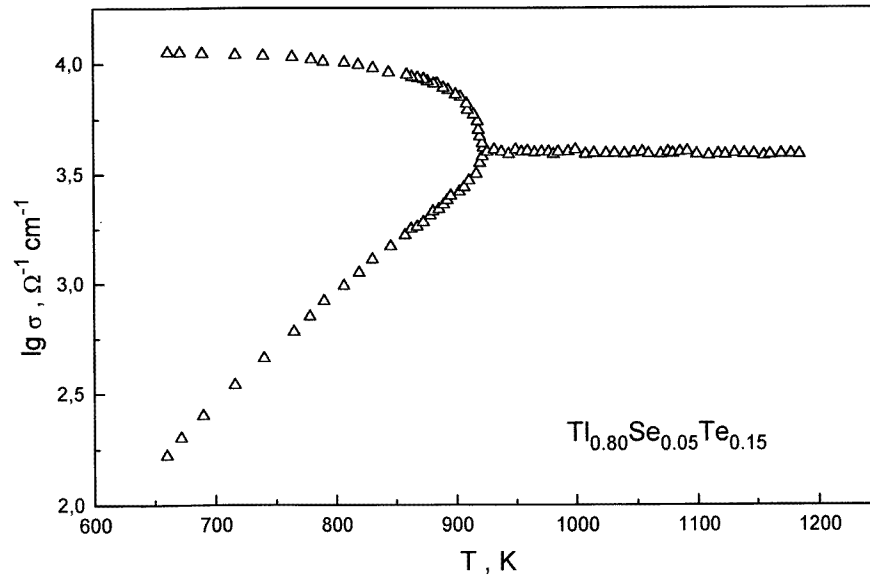


Figure 3. Temperature dependence of the electrical conductivity for the liquid $\text{Tl}_{0.80}\text{Se}_{0.05}\text{Te}_{0.15}$ alloy.

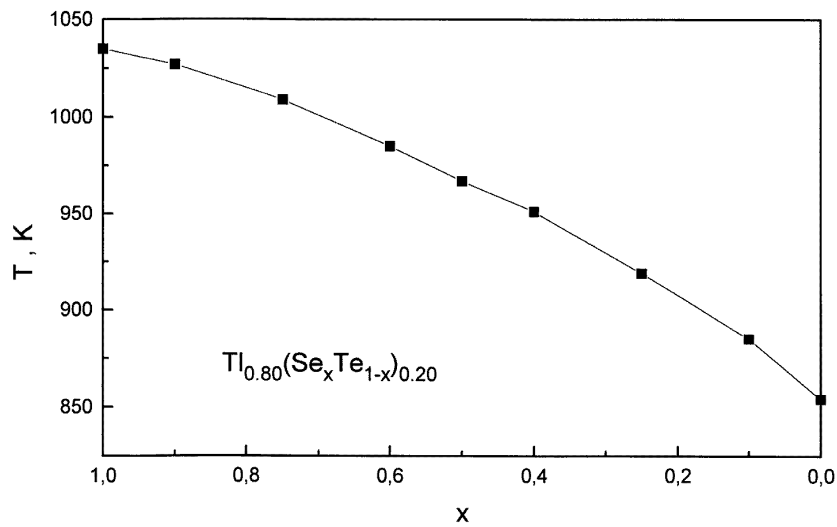


Figure 4. The phase separation temperatures of the liquid $\text{Tl}_{0.80}(\text{Se}_x\text{Te}_{1-x})_{0.20}$ alloys of different Se-to-Te ratios.

$T_S(x)$ on the Se-to-Te ratio for the alloys investigated is plotted in figure 4.

4. Discussion

In the absence of similar data available from the literature for ternary alloys, a comparative analysis of our results with those for binary immiscible Tl–Se and Tl–Te liquids seems to

be suitable and interesting. Phase diagrams of both systems expose the miscibility gaps from the Tl-rich side [1]. The critical temperatures of liquid–liquid coexistence were found to be equal to 1036 K for the Tl–Se system [6, 7] and 855 K for the Tl–Te system [8, 9]. Since the critical concentrations for both systems almost coincide and are equal to 19.7 at.% Se and 19.6 at.% Te, respectively, it seems reasonable to believe that the measured phase separation temperatures $T_S(x)$ reflect directly the behaviour of the critical point temperature during the transition from one binary system to the other, owing to the partial substitution of Se by Te. In other words, our data (figure 4) may be considered as those for a set of quasi-binary Tl–(Se/Te) alloys of almost critical concentrations. Moreover, the measured $\sigma(T)$ dependences (see figures 1–3) show the same behaviour as for binary alloys [7–9]. The $T_S(x)$ behaviour revealed does not show a linear dependence on the alloy composition and may have the following qualitative explanation. A simple mean-field model describing the liquid–liquid coexistence was proposed for binary metal alloys [10, 11]. Within the framework of pseudopotential formalism it was shown that the critical point parameters are mainly determined by the difference in the valences of the alloy components. In the case of the isovalent components the difference in the specific atom volumes or ‘effective’ ion-core radii dominates. However, a functional dependence of the critical concentration value x_c on these parameters is relatively weak, while the critical temperature varies approximately as $(r_a^2 - r_b^2)^2$, where r_a and r_b are the ‘effective’ ion-core radii of the components. Their absolute values are single fitting parameters in the respective pseudopotential expressions being used for the theoretical modelling. Unfortunately, similar calculations for the metal–chalcogen systems face many difficulties and seem to be impossible. However, the conclusions of the model provide a qualitative explanation of the peculiarities revealed in behaviour of the critical point parameters. In particular, Te and Se atoms have the same configuration of outer electron shells, but different nuclei charges and ion-core radii, which increase as the element number increases. If this is the case, then the x_c -values for binary Tl–Se and Tl–Te systems support the model. The weak dependence of the critical concentration on the ‘effective’ ion-core radii of the components, most probably, does not allow the experimental detection of a shift in the x_c -values at the partial substitution of Se by Te and transition from binary Tl–Se to quasi-binary $\text{Tl}_{0.80}(\text{Se}_x\text{Te}_{1-x})_{0.20}$ system alloys. On the other hand, however, even a weak change in the ‘effective’ ion-core radii of the chalcogen results in a substantial variation in the critical temperature due to the strong functional dependence mentioned above. Therefore the $T_S(x)$ -values decrease when the Te content in the Tl–Se–Te liquid alloys investigated increases.

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