Investigation of the critical region in monotectic systems by viscosity measurements

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Abstract. Viscosity measurements were performed for liquid In-Se alloys in the temperature-concentration range of a limited solubility. Critical parameters describing the peculiarities of the viscosity in the critical region are evaluated. The dynamic theory of phase transitions was used for this evaluation. The results are compared with previously obtained data for immiscible dielectric solutions and metallic melts.

1. Introduction

Binary monotectic alloys with a microstructure where soft phases are dispersed homogeneously in a hard matrix are of special technical importance [1]. These alloys are miscible at temperatures above the miscibility gap, but segregate into two liquids when they pass through the liquid miscibility gap. It is therefore very difficult to produce those alloys. The Stokes motion caused by the difference in densities of two liquids, and the Marangoni convection resulting from a temperature gradient (a liquid droplet moves to a higher temperature region in order to reduce the interfacial energy) are two main factors causing the separation of two immiscible liquids. In order to overcome the segregation, several techniques have been proposed aiming at producing a uniform dispersion of a softer phase in a harder matrix [2, 3]. The knowledge of the physical properties of the molten alloys prior to segregation is very important for the development of materials with predetermined characteristics. In this paper we present experimental studies of the viscosity of liquid In-Se alloys in the concentration-temperature range of the miscibility gap between 3 and 30 at. % of selenium. Viscosity essentially influences the velocity of the different phases separation processes and from this point of view viscosity data are of exceptional importance. Special attention has been focused on the behavior of the viscosity in the critical region of phase separation. The results are compared with previously obtained data for immiscible liquid metallic alloys and dielectric solutions.

2. Experimental

A computer-controlled oscillating-cup viscometer was used for viscosity, \( \eta(T) \), measurements [4]. Weighed (to within \( 10^{-4} \) g) amounts of In and Se (99.999 % purity) were melted in evacuated and sealed quartz ampoules. The initial compositions of the samples were accurate to 0.02 wt.%. The cylindrical quartz crucibles with internal diameters of 20 mm were used. After melting, the samples were homogenized for 4-5 h at the temperature of 1120 K. A homogeneous temperature field of 0.3 K has been created inside a furnace. The temperature was measured with the Pt/PtRh thermocouple arranged just below the crucible. The experiments were performed in an atmosphere of 90% Ar and
10% H₂ after initially pumping out the furnace working volume in order to avoid the oxidation of the sample. After the measurement the loss of the materials by vaporization did not exceed 0.4 %. Measurements were made starting from the maximal temperature with a cooling rate of 20 K/h, which was reduced to 2 K/h approaching to the segregation region. Using the modified Roscoe equation, \( \eta(T) \) was calculated from the logarithmic decrement and the period of oscillations [4]. The densities were calculated from the temperature dependences of the densities of pure components [5]. The viscosity values were obtained with an accuracy of about 3 %.

3. Results
The viscosity \( \eta(T) \) was measured for binary In\(_x\)Se\(_{100-x}\) alloys throughout the concentration range of the miscibility gap (3<x<30 at.%) between the binodal and 1120 K by five-percent steps. The results are shown in figure 1. Before the measurements the samples were kept 5-6 h at 1120 K for homogenization. Cooling the completely mixed melts is accompanied by an increase of the viscosity. \( \eta(T) \) adopts a maximum value if a gravitational phase separation of the melt in two liquid layers occurs. The observed cups correspond to the binodal temperatures, \( T_S \). The data obtained by further cooling should be understood as effective values and are omitted, for the sake of clarity. The absolute \( \eta(T) \) value in the high temperature region above the binodal is determined by the initial sample composition and increase when a Se content increases. The \( T_S \) values are presented in table 1 together with data determined earlier from the electrical conductivity [6], for comparison. Figure 2 represents the stratification curve for the In-Se system determined using viscosity and conductivity [6] data. The binodal temperatures determined by viscosity measurements are lower that those obtained earlier from the conductivity data [6]. Similar differences were noticed earlier for other monotectic systems (In-Te, Ga-Pb, In-Te-Tl), and possible sources of such differences were discussed in details in [7].

| In\(_{100-x}\)Se\(_x\), x = | 5  | 10 | 15 | 19 | 20 | 22 | 24 | 25 | 28 |
|----------------------------|----|----|----|----|----|----|----|----|----|
| \( T_S, K, \) el.cond.     | 829| 909| 943| 949,5| 949,3| 946,8| 934| 841,5|
| \( T_S, K, \) visc.        | 814| 881| 907|   |    |    |    |    |    |

Table 1. Binodal temperatures, \( T_S \), of the In-Se alloys

![Figure 1. Viscosity as a function of temperature of In-Se liquid alloys](image1)

![Figure 2. Miscibility gap of the In-Se system](image2)

4. Discussion
According to the dynamic theory of the critical phenomena [8-10], the viscosity of a liquid in the critical region is described by the following expression:

\[
\eta(T) = \eta_s(T) + \eta_f(T) = \eta_s(T)(q R_c)^2 = \eta_s(T)(r_0 q)^2 1^{1/2}
\]  

(1)
where \( \eta_b(T) = A \exp(B/T) \) is a regular part of viscosity and \( \eta_f(T) \) is a fluctuation viscosity. \( R_c = r_0 t^n \) is a correlation length of the concentration fluctuations, \( r_0 \) is a system-dependent amplitude. \( n \) denotes a critical exponent of the correlation length, and \( z \) is a critical exponent of viscosity. \( q \) is a wave number, \( t = (T - T_c)/T_c \). As is seen from equation (1), \( \eta(T) \) of a liquid tends to infinity if \( T \) approaches \( T_c \) \((t \to 0)\). The analysis of this formula reveals that the temperature region of its application is limited. It cannot be applied in the hydrodynamic region, where \( qR_c << 1 \). On the other hand, a temperature region of its reliable application as \( t \to 0 \) is also not determined. Moreover, the analysis of the available experimental data indicates that viscosity takes a finite value at the critical point [11-14].

This suggestion follows also from the model of Fixman developed in his studies as early as 1960th [15], where a spatial dispersion near critical point was taken into account. Nevertheless, a rather complicated Fixman viscosity equation as well as other analytical expressions for transport coefficients proposed later (e.g. in [16]) can hardly be applied for metallic melts, as they often contain a number of unknown parameters like diffusion constants, chemical potentials, osmotic pressures etc. [15]. In a simplified solution of the viscosity equation [15], the fluctuation viscosity \( \eta_f(T) \) is connected to the compressibility \( \beta \) and the correlation length as \( \eta_f(T) \sim \beta^{1/2} \sim R_c \sim t^{1/2} \).

Based on the Fixman theory, a semiempirical viscosity equation has been proposed [12]. In the present work we use a modified expression for the fluctuation viscosity which takes account of the spatial dispersion of the system near \( T_c \) by a quadratic term \((qR_c)^2\) [17]:

\[
\eta_f = \left[ \frac{(AR_c)^2}{1 + (qR_c)^2} \right]^{1/2} = \left[ \frac{(\Delta \eta_0 t^{-\nu})^2}{1 + (qR_c^{-\nu})^2} \right]^{1/2}
\]

where \( \Delta \eta_0 \) is an amplitude of the singular viscosity. This formula agrees with the Fixman equation, assures viscosity finiteness at the critical point and was already approved for different binary immiscible systems [11-14]. Over a wide range of temperatures, including the vicinity of the \( T_c \), the viscosity can be approximated by:

\[
\eta(T) = \eta_b(T) + \eta_f(T) = A \exp\left( \frac{B}{T} \right) + \left[ \frac{(\Delta \eta_0 t^{-\nu})^2}{1 + (qR_c^{-\nu})^2} \right]^{1/2}
\]

The viscosity of the critical composition In\(_{80}\)Se\(_{20}\) is presented in figure 3.

**Figure 3.** Temperature dependence of the viscosity in liquid In\(_{80}\)Se\(_{20}\): ○ experimental, – calculated by Eq. (3) with fitting parameters from Table 2, --- background viscosity obtained with \( A = 0.317 \) mPa s, \( B = 1227 \) K.

The application of equations (1) and (3) allows to calculate important parameters characterizing the viscosity near \( T_c \): \( \Delta \eta_0 \), \( qR_0 \), \( n \), and \( \eta_b \) being defined as \( \Delta \eta_0 / qR_0 \). As a first step, the parameters \( A \) and \( B \) of the background viscosity were deduced from the high temperature region \((t > 10^5)\) where \( \eta_b(T) >> \eta_f(T) \). This contribution is represented by the dashed line in figure 3. With the help of the
experimental viscosity, the singular viscosity was calculated according to \( \eta_s(T) = \eta(T) - \eta_s(T) \). The further analysis of this part was conducted by considering the temperature dependence of \( \Delta \eta_s = (\eta_s(T) - \eta_s(0)) \sim \tau^{\nu} \) in a double logarithmic scale. \( n \) was found to be 0.63 ± 0.05 which is a value close to the universal exponent of the correlation length 0.63 [18]. \( z_n \) was determined from the temperature dependence of \( \eta(T)/\eta_s(T) \) in a double logarithmic scale. Therewith it was possible to find a value of \( z_n \nu = 0.0429 \). Using now \( \nu = 0.64 \) the critical exponent of viscosity turned out to be 0.067 ± 0.005. The critical parameters found for In\(_{80}\)Se\(_{20}\) are collected in table 2 together with those of other binaries.

| System            | \( A \) (mPa s) | \( \Delta \eta_0 \) (mPa s) | \( \eta_0 \) (mPa s) | \( B \) (K) | \( n \)     | \( (qr_0) \) | \( z_\eta \) |
|-------------------|-----------------|-----------------------------|----------------------|-------|---------|------------|---------|
| In\(_{80}\)Se\(_{20}\) | 0.317           | 0.29Ã—10\(^{-2}\)          | 0.256                | 1227  | 0.64 + 0.03 | 0.003      | 0.067 + 0.005 |
| Ga\(_{31}\)Pb\(_{48.5}\) | 0.432           | 0.279Ã—10\(^{-2}\)         | 0.279                | 922.4 | 0.62 + 0.03 | 0.01       | 0.065 + 0.005 |
| In\(_{80}\)Se\(_{20}\)Tl\(_40\) | 0.205           | 0.16Ã—10\(^{-2}\)          | 0.05                 | 1799  | 0.63 + 0.05 | 0.032      | 0.068 + 0.005 |
| In\(_{30}\)Te\(_{20}\)Tl\(_{10}\) | 0.224           | 0.26Ã—10\(^{-2}\)          | 0.26                 | 999   | 0.63 + 0.02 | 0.02       | 0.063 + 0.005 |
| In\(_{80}\)Se\(_{20}\)Te\(_{16}\) | 0.34            | 0.29Ã—10\(^{-2}\)          | 0.29                 | 1200  | 0.63 + 0.03 | 0.01       | 0.063 + 0.005 |
| Methanol-heptane  | 0.02            | 0.29Ã—10\(^{-2}\)          | 0.097                | 911   | 0.63 + 0.05 | 0.03       | 0.06 + 0.007  |
| Methanol-hexane   | 0.02            | 0.19Ã—10\(^{-2}\)          | 0.095                | 878   | 0.61 + 0.05 | 0.02       | 0.06 + 0.007  |

A physical meaning of the reciprocal value of the wave number \( q^* \) can be now explained. As found from the molecular light scattering data, an amplitude of the correlation length \( \eta_s \) is equal to 1÷3 Å [12]. Based on the \( qr_0 \) values for different systems, collected in Table 2, \( q^* \) turned out to be \( \approx 100 \) Å. It is suggested that \( q^* \) is close to the correlation length of the liquid system at the border of the hydrodynamic region at \( t \approx 10^{-3} \). Comparing the critical parameters, it is revealed that the universality principle spreads to such the different materials as dielectric demixing solutions and metallic melts.

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