ELSEVIER

Journal of Alloys and Compounds 452 (2008) 174–177

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Viscosity of liquid In–Se–Tl alloys in the miscibility gap region

Yu. Plevachuk[a,*], V. Sklyarchuk[a], O. Alekhin[b], L. Bulavin[b]

[a] *Ivan Franko National University, Department of Metal Physics, Kyrylo and Methodiy Strasse, 8, 79005 Lviv, Ukraine*
[b] *Kyiv National Taras Shevchenko University, Faculty of Physics, 03022 Kyiv, Ukraine*

Received 18 September 2006; received in revised form 10 December 2006; accepted 21 December 2006

Abstract

The shear viscosity measurements were performed for liquid $In_xSe_{20}Tl_{80-x}$ ($0 \leq x \leq 80$ at.%) alloys over a wide temperature range above the monotectic using an oscillating-cup viscometer. In this range the ternary In–Se–Tl system may be considered as a set of “quasibinary” immiscible metal-chalcogen alloys of critical composition. Variation of the In/Tl ratio at a constant Se content changes the properties of the coexisting liquids and affects the temperature of demixing. The critical parameters describing the peculiarities of the viscosity behavior in the vicinity of the critical point are evaluated. Based on the dynamic theory of phase transitions a description of the viscosity in the region of phase separation is proposed. The results are compared with available data for immiscible dielectric solutions and metallic melts.

PACS: 64.60.Fr; 64.75.+g; 66.20.+d

Keywords: Metals and alloys; Electronic properties; Phase diagrams; Phase transitions; Viscosity

---

1. Introduction

Monotectic alloys with a microstructure where soft phases are dispersed homogeneously in a hard matrix have great potential applications [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 such alloys. There are two important factors that cause the separation of two immiscible liquids. One is Stokes’ motion caused by the density difference between two liquids, and the other is the Marangoni motion resulting from a temperature gradient, i.e. the liquid droplet moves to a higher temperature region in order to reduce the interfacial energy. In order to overcome these factors of segregation in immiscible alloys, several techniques have been proposed aiming at producing a uniform dispersion of a softer phase in a harder matrix [2,3].

At this point, 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–Tl alloys in the concentration–temperature range of the miscibility gap. Viscosity essentially influences the velocity of the different phase 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.

2. Experimental

Viscosity was measured using a computer-controlled oscillating-cup viscometer [4]. Weighed (to within 10^{-4} g) amounts of In, Tl and Se (99.999% purity) with a total mass of about 70 g were melted in evacuated and sealed quartz ampoules. The initial compositions of the sample 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 a temperature of 1120 K. A homogeneous temperature field of 0.3 K has been created inside the furnace. The temperature has been measured with a Pt/PtRh thermocouple arranged just below the crucible. The experiments were performed in an atmosphere of 90% Ar and 10% H_2 after initially pumping out the working volume of the furnace in order to avoid the oxidation of the sample. After the measurement the weight of the sample was checked and the loss of material 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 on approaching the segregation region. Using the modified Roscoe equation, the dynamic viscosity has been calculated from the logarithmic decrement and the period of oscillations

---

[*] Corresponding author. Tel.: +38 32 2964594; fax: +38 32 2631565.
E-mail address: plevachuk@mail.lviv.ua (Yu. Plevachuk).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.12.160

[4]. The required density values were calculated from the temperature dependences of the densities of the pure components [5]. The viscosity values were obtained with an accuracy of about 3%.

3. Results

The viscosity measurements were performed on ternary $In_xSe_{20}Tl_{80-x}$ alloys where $x = 0$, 10, 20, 30, 40, 50, 60, 70, 80. The results for some selected melts are shown in Fig. 1. As can be seen, cooling the completely mixed melts is accompanied by an increase of the viscosity according to the Arrhenius equation. The viscosity, $\eta(T)$, adopts a maximum value if a gravitational phase separation of the melt in two liquid layers occurs. The observed cusps correspond to the binodal temperature points T_S. The data obtained by further cooling should be understood as effective values. The onset of the melt solidification at the monotectic temperature T_M was found to be indicated by a pronounced change in the logarithmic decrement.

The absolute viscosity values in the high temperature region above the binodal are determined mainly by the initial sample composition and increase from $In_{80}Se_{20}$ to $Se_{20}Tl_{80}$. The binodal temperature depends strongly on the In/Tl ratio and changes in a nonlinear manner with a maximum at $In_{20}Se_{20}Tl_{60}$. The concentration dependencies of the binodal T_S and monotectic T_M temperatures determined from viscosity measurements as well as former results obtained from electrical conductivity investigations [6] are shown in Fig. 2. The data are collected in Table 1.

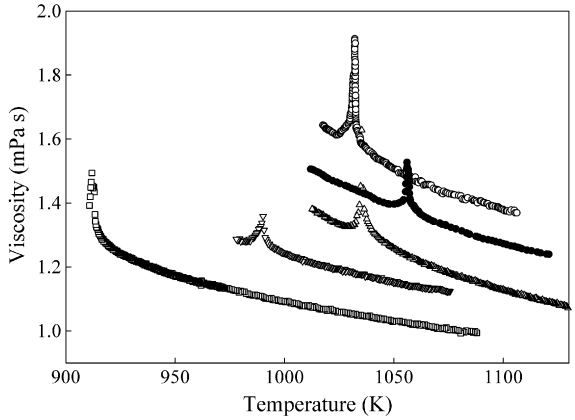

Fig. 1. Viscosity vs. temperature of In–Se–Tl liquid alloys: (○) $Se_{20}Tl_{80}$, (●) $In_{20}Se_{20}Tl_{60}$, (△) $In_{40}Se_{20}Tl_{40}$, (▽) $In_{60}Se_{20}Tl_{20}$, (□) $In_{80}Se_{20}$.

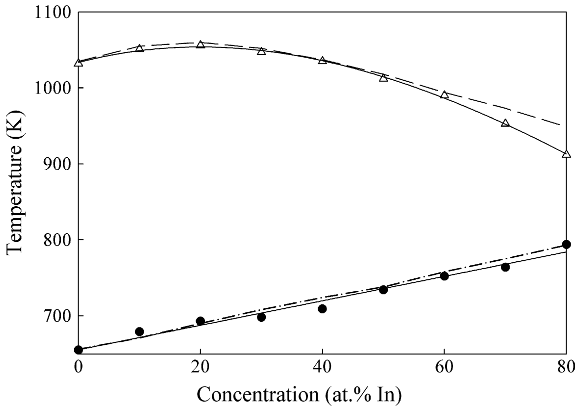

Fig. 2. Binodal and monotectic temperatures of $In_xSe_{20}Tl_{80-x}$ melts vs. content of indium. (△, —) Binodal from viscosity and electrical conductivity [6]; (●, - · -) monotectic from viscosity and electrical conductivity [6].

Table 1
Experimental data on binodal and monotectic temperatures of the system In–Se–Tl

Composition	Binodal temperature T_S (K)	Monotectic temperature T_M (K)
$Se_{20}Tl_{80}$	1032 ± 2	655 ± 1.5
$In_{10}Se_{20}Tl_{70}$	1051 ± 2	679 ± 1.5
$In_{20}Se_{20}Tl_{60}$	1056 ± 2	693 ± 1.5
$In_{30}Se_{20}Tl_{50}$	1047 ± 2	698 ± 1.5
$In_{40}Se_{20}Tl_{40}$	1035 ± 2	709 ± 1.5
$In_{50}Se_{20}Tl_{30}$	1012 ± 2	734 ± 1.5
$In_{60}Se_{20}Tl_{20}$	990 ± 2	752 ± 1.5
$In_{70}Se_{20}Tl_{10}$	953 ± 2	764 ± 1.5
$In_{80}Se_{20}$	912 ± 2	794 ± 1.5

4. Discussion

Investigations of the miscibility gap region in the systems In–Se [7] and Se–Tl [8] by electrical conductivity experiments revealed that the critical composition of both binaries consists of approximately 80 at.% metal and 20 at.% Se. Above the critical temperature T_c (912 K for $In_{80}Se_{20}$ and 1032 K for $Se_{20}Tl_{80}$) both systems are completely miscible at all compositions in the liquid state. The difference in the values of T_c could be due to the difference in atomic radii and different bonding conditions [1].

By changing the content of selenium in the In–Se–Tl alloys from 15 to 25 at.% Se we found that the composition with 20 at.% Se had the highest phase separation temperature. It was suggested that the ternary $In_xSe_{20}Tl_{80-x}$ system may be considered as a set of the "quasibinary" immiscible In/Tl–Se alloys. There is good reason to believe that the binodal temperature T_S, determined during the transition from one binary system to the other due to the substitution of the In by Tl can be considered as a very close one to the critical temperature T_c.

The binodal line in Fig. 2 determined by viscosity measurements slightly differs from that obtained earlier from the electrical conductivity data [6]. Similar small differences were noticed earlier for other monotectic systems (In–Te, Ga–Pb, In–Te–Tl), and possible sources of such differences were discussed in detail in [9]. In a previous paper such a maximum in the binodal temperature was explained by a simple mean-field theory and the Bancroft and Timmermans rule [6].

According to the dynamic theory of the critical phenomena [10–12], the viscosity of a liquid in the critical region is described by the following expression:

$$\eta(T) = \eta_r(T) + \eta_f(T) = \eta_r(T)(qR_c)^{Z\eta} = \eta_r(T)(r_0 q)^{Z\eta} t^{-\nu Z\eta} \tag{1}$$

where $\eta_r(T) = A\exp(B/T)$ is a background or regular part of viscosity, and $\eta_f(T)$ is a singular or fluctuation viscosity. $R_c = r_0 t^{-\nu}$

Table 2
Critical parameters of liquid $In_{40}Se_{20}Tl_{40}$ compared to other systems

System	A (mPa s)	$\Delta\eta_0$ (mPa s)	η_{fc} (mPa s)	B (K)	ν	(qr_0)	z_η
$In_{40}Se_{20}Tl_{40}$	0.205	0.16×10^{-2}	0.05	1799	0.63 ± 0.05	0.032	0.068 ± 0.005
$In_{30}Te_{20}Tl_{50}$	0.224	0.26×10^{-2}	0.26	999	0.63 ± 0.02	0.02	0.063 ± 0.005
$In_{80}Se_{04}Te_{16}$	0.34	0.29×10^{-2}	0.29	1200	0.63 ± 0.03	0.01	0.063 ± 0.005
$Ga_{51.5}Pb_{48.5}$	0.432	0.279×10^{-2}	0.279	922.4	0.62 ± 0.03	0.01	0.065 ± 0.005
Methanol–heptane	0.02	0.29×10^{-2}	0.097	911	0.63 ± 0.05	0.03	0.06 ± 0.007

is a correlation length of the concentration fluctuations, r_0 is a system-dependent amplitude. ν denotes a critical exponent of the correlation length, and z_η is a critical exponent of viscosity. q is a wave number, $t = (T - T_c)/T_c$.

As is seen from Eq. (1), the viscosity of a liquid tends to infinity if T approaches to 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 $qR_c \ll 1$. 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 [13–16].

This suggestion follows also from the model of Fixman developed in his studies as early as 1960 [17,18], 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 [19]) can hardly be applied to metallic melts, as they often contain a number of unknown parameters like diffusion constants, chemical potentials, osmotic pressures, etc. [17]. In a simplified solution of the viscosity equation [17], the fluctuation viscosity $\eta_f(T)$ is connected linearly to the compressibility β 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 [15]. In the present work, we use a modified expression of the fluctuation viscosity which takes account of the spatial dispersion of the system near T_c by a quadratic term $(qR_c)^2$ [20]:

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

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 [13–15].

Over a wide range of temperatures, including the vicinity of the T_c, the viscosity can be approximated by:

$$\eta(T) = \eta_r(T) + \eta_f(T) = A \exp\left(\frac{B}{T}\right) + \left[\frac{(\Delta\eta_0 t^{-\nu})^2}{1+(qR_c)^2}\right]^{1/2} \qquad (3)$$

The viscosity of the alloy $In_{40}Se_{20}Tl_{40}$ in the temperature region including the critical range is presented in Fig. 3. The application of Eqs. (1) and (3) allows to calculate important parameters characterizing the viscosity near T_c: $\Delta\eta_0$, qr_0, ν, z_η, and η_{fc} 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 ($t > 10^{-2}$) where $\eta_r(T) \gg \eta_f(T)$. This contribution is represented by the dashed line in Fig. 3. With the help of the experimental viscosity, the singular viscosity was calculated according to $\eta_f(T) = \eta(T) - \eta_r(T)$. The further analysis of this part was conducted by considering the temperature dependence of $\Delta\eta_f^{-1} = (\eta_f^{-1} - \eta_{fc}^{-1}) \sim t^n$ 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 [21]. z_η was determined from the temperature dependence of $\eta(t)/\eta_r(t)$ in a double logarithmic scale. Therewith it was possible to find a value of $z_\eta \nu = 0.043$. Using now $\nu = 0.63$ the critical exponent of viscosity z_η turned out to be 0.068 ± 0.005. The critical parameters found for $In_{40}Se_{20}Tl_{40}$ are collected in Table 2 together with those of other binaries [14,15].

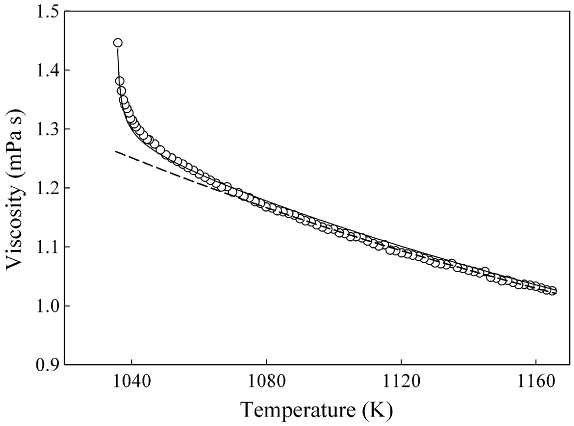

Fig. 3. Temperature dependence of the viscosity in liquid $In_{40}Se_{20}Tl_{40}$: (○) experimental, (—) calculated by Eq. (3) with fitting parameters from Table 2, (- - -) background viscosity obtained with $A = 0.205$ mPa s, $B = 1799$ K.

A physical meaning of the reciprocal value of the wave number q^{-1} can be now explained. As found from the molecular light scattering data, an amplitude of the correlation length r_0 takes the values between 1 and 3 Å [15]. Based on the qr_0 values for different systems collected in Table 2 q^{-1} turned out to be ≈100 Å. It is suggested that q^{-1} is close to the correlation length of the liquid system at the border of the hydrodynamic region at $t \approx 10^{-3}$. Finally, comparing the values of the critical parameters it is indicated that the universality principle spreads out to such the different materials as immiscible metallic melts and dielectric demixing solutions.

5. Conclusion

An expression assuming the finiteness of the viscosity value at the critical point was deduced. The experimental data were approximated by a new equation for the temperature dependence of viscosity over a wide range of temperature, which included also the vicinity of the critical point. The critical parameters describing the peculiar behavior of the viscosity in the critical region were estimated.

Acknowledgments

The authors Yu. Plevachuk and V. Sklyarchuk acknowledge the support of this work by the Deutsche Akademische Austauschdienst (DAAD).

References

[1] L. Ratke, S. Diefenbach, Mater. Sci. Eng. R 15 (1995) 261.
[2] F. Oeters, in: L. Ratke (Ed.), Immiscible Liquid Metals and Organics, DGM Informationsgesellschaft, Verlag, 1993, p. 261.
[3] B. Prinz, A. Romero, in: L. Ratke (Ed.), Immiscible Liquid Metals and Organics, DGM Informationsgesellschaft, Verlag, 1993, p. 281.
[4] J. Vollmann, F. Herwig, M. Wobst, Exp. Techn. Phys. 39 (1991) 527.
[5] T. Iida, R.I.L. Guthrie, The Physical Properties of Liquid Metals, Clarendon Press, Oxford, 1993.
[6] Yu. Plevachuk, V. Didoukh, B. Sokolovskii, J. Phase Equilibria 20 (4) (1999) 404.
[7] V. Didoukh, Yu. Plevachuk, B. Sokolovskii, J. Phase Equilibr. 17 (5) (1996) 414.
[8] B. Sokolovskii, V. Didoukh, M. Wobst, W. Hoyer, Phys. Stat. Sol. (a) 139 (1993) 153.
[9] Yu. Plevachuk, V. Filippov, V. Kononenko, et al., Z. Metallkd. 94 (9) (2003) 1034.
[10] L.P. Kadanoff, J. Swift, Phys. Rev. 166 (1) (1968) 89.
[11] B.I. Halperin, P.C. Hohenberg, Phys. Rev. 177 (2) (1969) 952.
[12] R.A. Ferrell, Phys. Rev. Lett. 24 (1970) 1169.
[13] A.V. Oleinikova, L.A. Bulavin, V. Pipich, Chem. Phys. Lett. 278 (1997) 121.
[14] A. Alekhin, V. Sperkach, B. Abdykarimov, O. Bilous, Ukr. J. Phys. 45 (9) (2000) 1067.
[15] A. Alekhin, Ukr. J. Phys. 49 (2) (2004) 138.
[16] Yu. Plevachuk, V. Sklyarchuk, O. Alekhin, L. Bulavin, J. Phys. Stud. 9 (4) (2005) 333.
[17] M. Fixman, J. Chem. Phys. 36 (1962) 310.
[18] M. Fixman, J. Chem. Phys. 36 (1962) 1961.
[19] R. Folk, G. Mozer, Condens. Matter. Phys. 7 (1996) 27.
[20] L.D. Landau, E.M. Lifshitz, Statistical Physics, Butterworth-Heinemann, Oxford, 1980.
[21] A. Patashinskii, V. Pokrovskii, Fluctuation Theory of Phase Transitions, Nauka, Moskow, 1982.