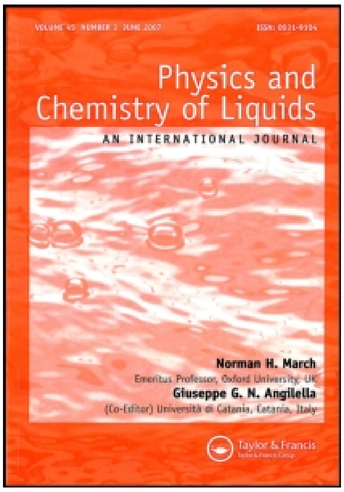

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The structure and viscosity features in In–Bi near-eutectic melts

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The $In_{1-x}Bi_x$ ($x = 0.40, 0.34, 0.23, 0.13, 0.09$) molten alloys have been studied by means of viscosity measurements and X-ray diffraction method. Temperature dependence of viscosity coefficient shows the Arrhenius like behavior with anomalous in form of local maximum and significant scattering of experimental values. The features in temperature dependencies of viscosity coefficient were studied also by means of X-ray diffraction method.

Keywords: Molten alloys; Structure of melts; Viscosity; Indium–Bismuth; X-ray diffraction; Eutectic

1. Introduction

The diffraction studies and physical properties measurements reveal the existence of microsegregations in binary alloys with eutectic point in phase diagram [1]. It was established by theoretical studies [2] that at cooling of alloy, considered as a regular solution to eutectic temperature reveals the thermodynamic instability. The region of such instability can be estimated by means of theoretical approaches. Authors of these studies concluded that significant fluctuations or formation of inhomogeneities accompanies transition in such solutions at cooling from metastable state to nonregular one. At further cooling, the drastic change in atomic arrangement occurs.

Certainly that anomalous behavior of physical properties and structure is expected to be pronounced at such transition [3]. Unfortunately the systematic studies on this interesting problem are rather poor. The viscosity coefficient temperature dependence is analyzed commonly in order to estimate the structure changes in liquid state. The deviation of experimental data from Arrhenius like behavior is the main evidence of structure transformation. But the information about such processes taken from

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viscosity data only is not sufficient to make the complete conclusions. For this reason we have combined the X-ray diffraction investigation with viscosity coefficient measurement. For studying structure changes, the In–Bi near-eutectic liquid alloys were chosen.

The available diffraction studies of molten alloys of this system [4] show that their structure, especially InBi and In_2Bi liquid chemical compounds is characterized by chemical ordering of In and Bi atoms, but there are no conclusions about atomic arrangement in molten alloys of other concentrations.

The equilibrium phase diagram of In–Bi binary system reveals the existence of In_2Bi, In_3Bi_5, and InBi chemical compounds. In_2Bi and In form the eutectic alloy. Negative values of enthalpy of mixing especially in In-rich part and existence of chemical compounds phase diagram [5] indicate the tendency to preferred interaction of unlike kind atoms, but the thermal stability of these compounds upon melting is supposed to be low. Taking into account the features of In–Bi phase diagram we assume that concentration fluctuations can be revealed in behavior of properties and structure of near-eutectic melts.

2. Experimental

Samples were prepared in arc melting furnace filled with pure argon from In and Bi of 99.999% purity. The diffraction studies were carried out using a high-temperature diffractometer with a special attachment that allows investigating the liquid samples at different temperatures up to 1800 K. Cu–K_α radiation monochromatized by means of LiF single crystal as a monochromator and Breg–Brentano focusing geometry were used. The scattered intensity for different scattering angles were recorded within the range $1\,\text{Å}^{-1} < k < 7\,\text{Å}^{-1}$, with different angular step, which was equal to 0.05° within the region of principal peak and 0.5° at rest values of scattering angles. The scattered intensity was measured with accuracy, better then 2%. In order to obtain the scattered intensities of such accuracy, the scan time was selected to be 100 s. The diffracted intensity was recorded using a NaI(Tl) scintillator detector in conjunction with an amplification system. The sample was placed in a rounded cup of 20 mm diameter. Intensity curves were corrected on polarization and incoherent scattering [6]. After this procedure they were normalized to electron units by Krogh–Moe method [7]. Obtained intensity curves were used to calculate the structure factors (SF) and then the pair correlation function (PCF). Main structure parameters, obtained from SF and PCF were analyzed.

The oscillating crucible method was used for measuring the viscosity. The period and logarithmic decrement of the oscillations were measured by means of optical system. In order to obtain the viscosity coefficient from the measured logarithmic decrement data, Shvidkovski equation has been used [8]. The experiments were performed in a helium atmosphere after initial pumping. The accuracy of measurements was less than 3%.

3. Results and discussion

The temperature dependence of viscosity for molten $In_{1-x}Bi_x$ ($x = 0.40, 0.34, 0.23, 0.13, 0.09$) alloys is shown in figure 1. Concentrations of these

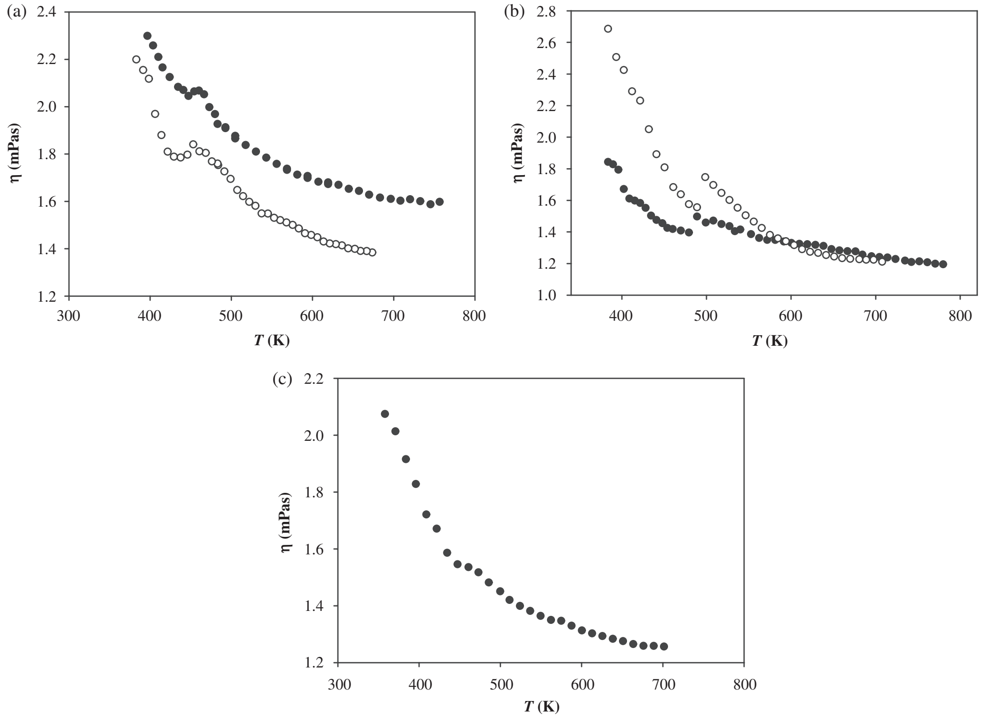

Figure 1. The temperature dependencies of viscosity (a) $In_{0.91}Bi_{0.09}$ (○),$In_{0.87}Bi_{0.13}$ (●); (b) $In_{0.66}Bi_{0.34}$ (○), $In_{0.60}Bi_{0.40}$ (●); (c) $In_{0.77}Bi_{0.23}$.

melts correspond to various composition of In_2Bi–In eutectic subsystem. As it can be seen from figure 1, the temperature dependence of viscosity coefficient for each of these molten alloys is generally characterized by exponential function. Nevertheless, the significant deviation from this function is observed. For example, in case of melt containing 91 at.% In the local maximum is pronounced at $T = 450$ K. Some increase of viscosity is also observed in temperature region 600–800 K. With increase of Bi content the similar tendency persists, but there is a significant scattering of experimental data.

For eutectic melt the deviation from exponential curve is less compared to others (figure 1c). For liquid In_2Bi chemical compound, as a constituent of eutectic system, the local maximum in temperature dependence of viscosity is revealed at temperature about 500 K.

Therefore, the analysis of viscosity temperature dependencies allowed us to conclude that the reason of anomalous behavior is supposed to be caused by the structure changes in these melts. It is known from experimental data [9] that some deviation of viscosity from Arrhenius-like dependence is observed for semi-metals (Sn, Bi, Ga, and others). Such behavior is attributed to existence of some temperature interval where two kinds of structures coexists. Upon melting some part of atoms with covalent bonding persists that influences the viscosity coefficient value.

In order to confirm the assumption about structure change we have also studied the melts containing 87 and 77 at.% In by means of X-ray diffraction method. The structure factors obtained for these alloys and compared with ones for liquid Bi and In

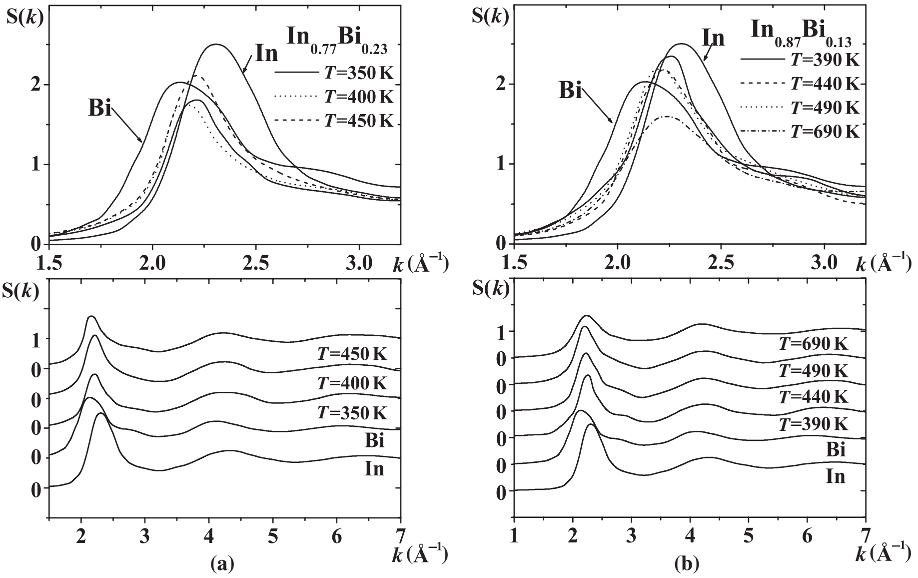

Figure 2. Structure factors for $In_{0.77}Bi_{0.23}$ (a) and $In_{0.87}Bi_{0.13}$ (b) molten alloys.

are shown in figure 2. Principal peak details are also shown in top of figure 2. As it can be seen the experimental SF shows the profile, which is significantly different from one of liquid In although its content prevails in both alloys. The addition of Bi atoms is very active in change of atomic distribution of In. Principal peak position k_1 is shifted to small k-value and the shoulder on right-hand side of this peak is revealed as in one for liquid Bi. Therefore, the molten $In_{0.87}Bi_{0.13}$ and $In_{0.77}Bi_{0.23}$ alloys significantly deviates from molten solution with random atomic distribution. Existence of shoulder allowed us to suppose that chemically ordered microgroups are the main structural units who are responsible for such deviation.

Important conclusion also can be drawn by comparing $g(r)$ functions for two near-eutectic melts with coordination numbers $N(r)$ depending on interatomic distances for crystalline In_2Bi and InBi compounds (Figure 3). As it can be seen in figure 3, the better agreement between maxima positions is for In_2Bi compound. Atomic-arrangement-like structure of this compound exists also at higher temperatures showing the influence of chemical short-range order on atomic distribution.

The structure parameters obtained from SF and pair correlation functions for indium, bismuth and alloys of In–Bi system are listed in table 1. It is known that for most of liquid metals and their alloys commonly the increase of most probable interatomic distance r_1, decrease of SF principal peak height $S(k_1)$, and increase of the half height width (Δk) are observed. Such behavior indicates the structure disordering in melts, which approximately can be considered as simple liquids. In our case some deviation from the typical behavior occurs. In fact, the principal peak positions k_1, k_2 are unchangeable with temperature. No significant changes are observed for most probable interatomic distances r_1, r_2. It can be easily shown that all these parameters change linearly according to additive low in assumption that studied molten alloys are In-enriched solutions.

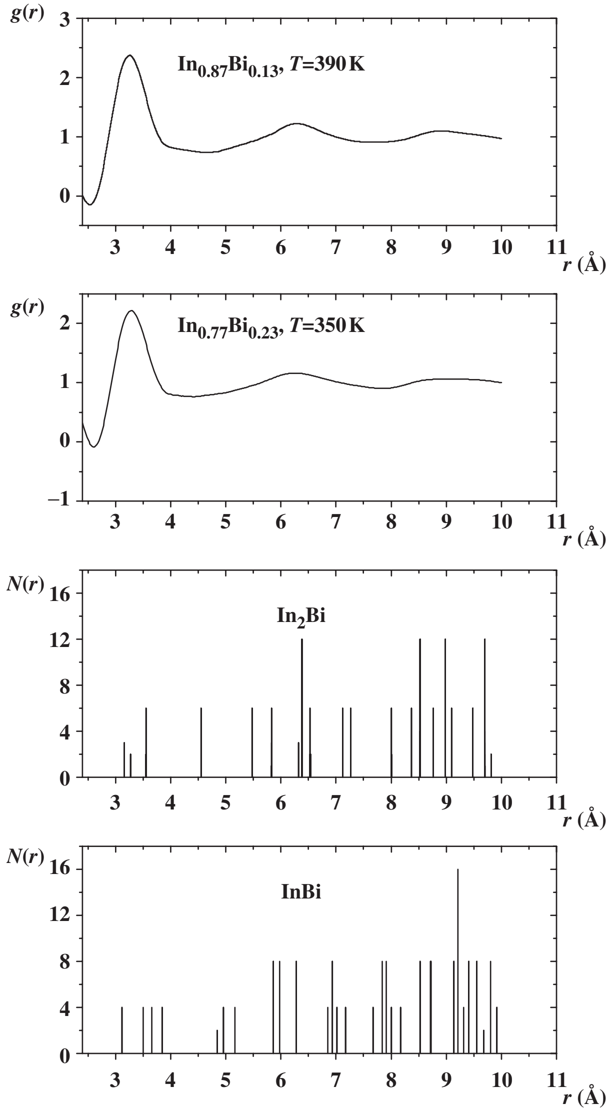

Figure 3. Pair correlation functions for liquid $In_{0.77}Bi_{0.23}$, $In_{0.87}Bi_{0.13}$ and coordination numbers $N(r)$ depending on interatomic distances for crystalline In_2Bi and InBi compounds.

Another structure parameter Δk relates to correlation radius: $L = 2\pi^3/2{,}5^2\Delta k$. The correlation radius is the distance from any initial atom to that one, where the correlation between them disappears. Commonly the correlation radius is considered as a size of structural units (clusters). This parameter can be also estimated from pair correlation function as a distance where the amplitude of maximum in $g(r)$ becomes less than 1 ± 0.02. Most of liquids show the decrease of correlation radius with heating that obviously occurs due to breaking of clusters and attempt to form the random atomic distribution. In our case, this parameter does not change within some temperature range at heating, showing the stability of structure, and then decreases figure 4.

Table 1. The main structure parameters obtained from structure factors and pair correlation functions.

T(K)	k_1(Å^{-1})	k_2(Å^{-1})	$S(k_1)$	Δk	r_1(Å)	r_2(Å)	Z
$In_{0.77}Bi_{0.23}$							
350	2.22	4.26	1.81	0.47	3.28	6.26	8.5
400	2.22	4.24	2.11	0.47	3.32	6.19	9.6
450	2.16	4.23	1.75	0.52	3.27	6.44	8.4
$In_{0.87}Bi_{0.13}$							
390	2.26	4.26	2.35	0.46	3.25	6.29	9.5
440	2.22	4.24	2.17	0.54	3.25	6.14	9.5
490	2.20	4.26	2.18	0.56	3.25	6.18	9.8
690	2.23	4.20	1.59	0.77	3.21	6.22	8.4
In	2.30	4.32	2.50	0.49	3.23	6.10	11.6
Bi	2.11	4.12	2.03	0.51	3.38	6.60	8.8

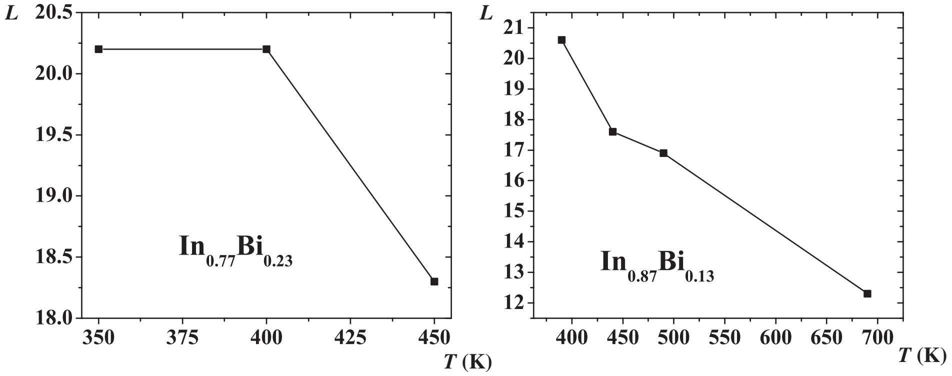

Figure 4. Temperature dependence of the correlation radius for $In_{0.77}Bi_{0.23}$ and $In_{0.87}Bi_{0.13}$ molten alloys.

Analyzing the X-ray data we can assert that studied In-based molten alloys are different than atomic solutions. It allows us to suppose the existence of clusters of two kinds: (1) In-enriched clusters where Bi-atoms are diluted; (2) chemically ordered In–Bi clusters.

Taking into account the thermodynamic data, physical properties concentration dependencies, and phase diagram, one can suppose that stoichiometry of chemically ordered clusters is In_2Bi. One can suggest that heating will promote the decrease of cluster stability due to more intensive atomic motion. In such case the structure parameters change in following way: k_1 parameter shifts to low k-values, structure factor principal peak decreases its height and correlation radius becomes less. The deviation from such behavior with earlier-mentioned features can be caused by some reasons. One of them which we consider, as the most probable is the high-thermal stability of chemically ordered structural units. Nevertheless, upon some temperature increase these atomic groups can be diluted with In-atoms without any significant change in structure. Due to this process a slight reduce of clusters size decrease can occur. Such atomic rearrangement also influences on interaction between each kind of clusters and is revealed on anomalous behavior of temperature dependence of viscosity. With heating some part of In atoms attempt to be diluted in In_2Bi clusters. During this process the topological and chemical short-range order in clusters transforms from In_2Bi-like kind to InBi one. Such process is accompanied with significant atomic diffusion and change of structural units size. In some temperature interval the increase of topological ordering degree and cluster aggregation can occur resulting the observed anomalous behavior in viscosity and structure parameters.

The assumption about existence of above mentioned structure, which is the metastable, is in accordance with results obtained by Popel [10] where it is shown that cluster (microdrop) radius increases with heating. Therefore, the transition of melt to homogeneous state is accompanied by concentration equalization in phases, which are in contact. At the same time the volume fraction of microdrops in melt increases. Only at higher temperature the diluting of microdrops is possible.

4. Conclusions

Viscosity for liquid $In_{1-x}Bi_x$ ($x = 0.40, 0.34, 0.23, 0.13, 0.09$) shows the features in its temperature dependence. The structure factors of liquid $In_{0.77}Bi_{0.23}$ and $In_{0.87}Bi_{0.13}$ near-eutectic melts show the anomalous dependence on temperature. The reason of such behavior is the microinhomogeneous atomic distribution where the chemically ordered In_2Bi clusters are located in indium based matrix. With heating the structure in clusters persists within temperature range up to 450 K. At higher temperatures the atoms of In-matrix attempt to be diluted in In_2Bi clusters changing their composition and structure.

References

[1] T. Massalsky (Ed.). *Binary Alloy Phase Diagrams*, 2nd Edn, ASM, Materials Park, OH (1990).
[2] E.V. Kalashnikov. *Tech. Phys.*, **42**, 4 (1997).
[3] P.S. Popel, E.L. Presnyakova, V.A. Pavlov, E.L. Arhangelskij. *Izv. Akad. Nauk SSSR. Metally*, **2**, 53 (1985).
[4] R. Bek, E. Nold, S. Steeb. *Z. Naturforsch. A*, **36**, 150 (1980).
[5] P.Y. Chevalier. *Calphad*, **12**(4), 383 (1988).
[6] D.T. Cromer, J.T. Waber. *Acta Cryst.*, **18**, 104 (1965).
[7] J. Krogh-Moe. *Acta Cryst.*, **9**, 951 (1956).
[8] E.G. Shvidkovski. *Nekotorye Voprosy Vyazkosti Rasplavlennych Metalov* [in Russian], Gostekhteorizdat, Moscow (1955).
[9] D. Wilson. *Structure of Liquid Metal Alloys* [in Russian], Mettalurgiya, Moscow (1972).
[10] P.S. Popel, E.L. Demina, E.L. Arhangelskij, B.A. Baum, G.V. Tyahunov, E.V. Kolotuhin. *Izv. Akad. Nauk SSSR. Metally*, **3**, 52 (1987).