VISCOSITY AND CONCENTRATION FLUCTUATIONS IN LIQUID In-Sb AND In-Bi ALLOYS

A. Yakymovych, V. Sklyarchuk, Yu. Plevachuk and S. Mudry
Ivan Franko National University, Physics of Metals Department, Kyrylo and Mephody St., 8, UA-79005 Lviv, Ukraine

Received: December 10, 2009

Abstract. The viscosity of liquid In-Sb and In-Bi molten alloys was studied in the region of InSb+Sb, InSb+In and In2Bi+In binaries. It was shown that InSb, In3Sb, and In2Bi – associates as well as self-associated In- and Sb-based atomic groups were responsible for anomalous temperature dependences of the viscosity coefficient. Changes in the structure and composition of structural units were supposed to be accompanied with concentration fluctuations in melts.

1. INTRODUCTION

It is known that most binary alloys are far from ideal solutions and reveal a microinhomogeneous atomic distribution. Various experimental methods have been used to study these inhomogeneities. Besides, models of an inhomogeneous structure have been also developed [1-3].

The existence of an inhomogeneous structure in liquid alloys within some temperature range is related to specific temperature dependences of structure and physical-chemical properties. For example, the anomalies of temperature dependences of the electrical conductivity within some temperature range upon melting [4].

It is also the structure studies that indicate that the most probable interatomic distance and number of neighbors deviate from those for a random atomic distribution, forming dynamical atomic groups of various compositions [5]. In liquid eutectic alloys and systems with a miscibility gap these microgroups behave similarly to atoms. It is only upon heating to higher temperatures that their size is reduced and an attempt to form the atomic solution is made. As follows from the data on neutron small angle scattering the size of these structural units at temperatures near the critical temperature is about 10 nm [6]. The change in these structural units size is accompanied by concentration fluctuation processes which influence many physical properties, particularly the viscosity.

The existence of an inhomogeneous structure has been also found in eutectic melts especially in those with an inflection point in the liquidus curve of the phase diagram. However, the literature data on concentration fluctuations in complex eutectic melts whose one component is a chemical compound are scarce.

The results on viscosity measurements of binary eutectic systems In-Sb and In-Bi are presented in this work. The compositions of the investigated alloys were chosen to be 87, 66, 77 at.% of In in In-Bi and 60, 50, 40 at.% In in In-Sb. Therefore these concentrations correspond to InSb and In2Bi chemical compounds and other alloys of InSb+In, InSb+Sb, In2Bi+In binary subsystems.
2. EXPERIMENTAL DETAILS

In our previous viscosity studies dedicated to these systems [7,8] the anomalies in all temperature ranges were revealed. In this work we attempted to interpret these results from the viewpoint of concentration fluctuations.

The viscosity coefficient was calculated to estimate the chemical ordering effect on the viscous properties. The calculations were carried out using the following formula [9]:

\[
\eta = \frac{2.408 \cdot 10^4 \mu^{1/3} (MT)^{1/2}}{1 - 1.8702 \mu^{1/3}},
\]

where \( \eta \) - the viscosity coefficient of liquid; \( \mu \) - the packing coefficient; \( M \) - the nuclear weight; \( V \) - the nuclear volume. The viscosity of alloys was calculated additively:

\[\eta = x_1 \eta_1 + x_2 \eta_2,\]

where \( \eta_1, \eta_2; x_1, x_2 \) were the viscosity coefficients of elements, atomic fractions and hard sphere diameters, respectively.

In order to confirm the suggestion about fluctuations of concentration, the mole fractions of the associates InSb and In\(_3\)Sb in the liquid state were also calculated.

It was assumed that the binary liquid In-Sb alloy consisted of a pseudo quaternary mixture of \( n_A \) and \( n_B \) moles of In and Sb atoms, and of \( n_{AB} \) and \( n_{A^2B} \) moles of two types of chemical complexes, InSb and In\(_3\)Sb, respectively. The total number of moles, \( n \), was given by

\[
n = n_A + n_B + n_{AB} + n_{A^2B},
\]

The absolute concentrations were obtained as \( x_A = n_A / N \) and \( x_B = n_B / N \) for 1 mole of a binary alloy (\( N=1 \)). Similarly, the following expressions could be written for the particle concentrations in the liquid:

\[
x_A = \frac{n_A}{n_A + n_B + n_{AB} + n_{A^2B}},
\]

\[
x_B = \frac{n_B}{n_A + n_B + n_{AB} + n_{A^2B}},
\]

\[
x_{AB} = \frac{n_{AB}}{n_A + n_B + n_{AB} + n_{A^2B}},
\]

\[
x_{A^2B} = \frac{n_{A^2B}}{n_A + n_B + n_{AB} + n_{A^2B}}.
\]

The chemical potentials \( \mu_\nu \) of the assumed species \( \nu \) (\( \nu = A_1, B_1, AB_i, A^2B_j \)) (for a review see reference [10]) were

\[
\mu_A = \mu_A^0 + RT \ln x_A = \mu_A^0 + RT \ln x_A \gamma_A,
\]

\[
\mu_B = \mu_B^0 + RT \ln x_B = \mu_B^0 + RT \ln x_B \gamma_B,
\]

where \( R \) was the gas constant, \( T \) the absolute temperature and \( \gamma \) the corresponding activity coefficient. From this it was possible to calculate the following:

Fig. 1. Viscosities of In\(_{60}\)Sb\(_{40}\) (a), In\(_{40}\)Sb\(_{60}\) (b), and In\(_{50}\)Sb\(_{50}\) (c), liquid alloys.
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Viscosity and concentration fluctuations in liquid In-Sb and In-Bi alloys

Fig. 2. Mole fraction of InSb and In$_3$Sb associates in liquid In-Sb alloys at 900K.

\[
\gamma_A = \frac{x_A}{x_A} \exp \left( \frac{\mu_A - \mu_A}{RT} \right),
\]
\[
\gamma_B = \frac{x_B}{x_B} \exp \left( \frac{\mu_B - \mu_B}{RT} \right),
\]  
(6)

For \( x_A \to 1 \), the effective mole fraction of the monomer molecules \( x_{A_1} \) tended to a limit \( x_{A_1} \) the mole fraction of monomers in the pure liquid, and so

\[
x_A^0 = \exp \left( \frac{\mu_A - \mu_A}{RT} \right),
\]
(7)

\[
\gamma_A = \frac{1}{x_A} x_A^0,
\]
(8)

and

\[
\gamma_B = \frac{1}{x_B} x_B^0
\]
(9)

was obtained in a similar way.

Since the pure components are usually non-associated in liquid metals, and since it did not seem reasonable to take into account more than two types of associates [11] \( x_{A_1} = 1 \) and \( x_{B_1} = 1 \) were obtained. With this the equations for activity coefficients could be rewritten:

\[
\gamma_A = \frac{x_A}{x_A},
\]
\[
\gamma_B = \frac{x_B}{x_B},
\]
(10)

This led to

\[
\gamma_A = \frac{x_A}{x_A} = \left(1 + \frac{\mu_A - \mu_A}{RT} \right),
\]
\[
\gamma_B = \frac{x_B}{x_B} = \left(1 + \frac{\mu_B - \mu_B}{RT} \right),
\]
(11)

\[
(\gamma_A) = \left(1 + \frac{\mu_A - \mu_A}{RT} \right) - \left(\frac{i x_{A_1} + i x_{A_B}}{x_A} \right).
\]
\[
(\gamma_B) = \left(1 + \frac{\mu_B - \mu_B}{RT} \right) - \left(\frac{j x_{B_1} + j x_{B_B}}{x_B} \right).
\]

The \( \gamma_A \) and \( \gamma_B \) values were taken from [12] to calculate the mole fractions of the associates.

3. RESULTS AND DISCUSSION

The measured viscosity coefficient values for molten alloys of an InSb+Bi(In) subsystem including InSb are shown in Fig. 1.

The \( d\eta/dT \) values calculated assuming a hard sphere model and the experimental values are also presented in the corner of this figure in order to determine more rather the anomalous behavior temperature region. As can be seen, all the temperature dependences reveal a deviation from the Arrhenius-like behavior. The hard sphere model predicts a slight decrease in \( \eta \) for molten InSb and a more significant decrease for the melt containing 60 at.% of Sb. Such a model is in disagreement with the experimental data showing that a most rapid reduction of viscosity occurs in a melt containing 40 at.% of Sb. It should be noted also that the liquidus curve in the equiatomic concentration region are flat that supposes large-concentration changes in the liquid at solidification because the concentrations of solid and liquid phases will be significantly different. Therefore, it can be supposed that a redistribution of components starts still before solidification in the liquid phase.

A small decrease in viscosity in molten InSb is supposed to be caused by significant InSb-like chemical ordering whereby the In and Sb concentration is close in solid and liquid states. Some part of InSb chemically ordered atomic groups dissociates upon melting and it is the first reason why the viscosity dependence deviates from the Arrhenius-like behavior.

The mole fractions of the InSb and In$_3$Sb associates in liquid alloys were also calculated to estimate the influence of such microgroups on the viscosity behavior (Fig. 2).
A small temperature range, where \( \frac{d\eta}{dT} \) is almost unchangeable for an equiatomic melt shows some thermal stability of chemical ordering upon melting. Such a temperature range is larger for a melt containing 60 at.% of Sb and does not exist in a melt with 40 at.% of Sb in which the alloy components are the InSb, InSb and In associates.

A smaller maximum in the phase diagram liquidus curve is observed in the In-Bi binary system and it corresponds to the In\textsubscript{2}Bi chemical compound. As in case of the In-Sb system the viscosity temperature dependences also reveal a deviation from the Arrhenius-like behavior (Fig. 3). An analysis of \( \frac{d\eta}{dT} \) shows that the hard sphere model is applicable at higher temperatures only. The experimental values of this parameter show large oscillations in the region of 450-550K for melts with a content of 87 and 66 at.% of In. Such oscillations are slight in case of liquid In\textsubscript{77}Sb\textsubscript{23}. The characteristic temperatures \( T_{ch} \) where the discrepancies between experimental and calculated \( \frac{d\eta}{dT} \) occur were found to be as shown in Table 1. These temperatures are

![Fig. 3. Viscosities of In\textsubscript{87}Bi\textsubscript{13} (a), In\textsubscript{66}Bi\textsubscript{34} (b), and In\textsubscript{77}Bi\textsubscript{23} (c), liquid alloys.](image)

![Fig. 4. Characteristic temperatures compared with equilibrium phase diagrams for In Bi (a) In Sb (b) system.](image)

**Table 1.** Characteristic temperature values.

<table>
<thead>
<tr>
<th>Melt composition</th>
<th>( T_{ch} ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>In\textsubscript{87}Bi\textsubscript{13}</td>
<td>504</td>
</tr>
<tr>
<td>In\textsubscript{66}Bi\textsubscript{34}</td>
<td>499</td>
</tr>
<tr>
<td>In\textsubscript{77}Bi\textsubscript{23}</td>
<td>501</td>
</tr>
<tr>
<td>In\textsubscript{60}Sb\textsubscript{40}</td>
<td>956</td>
</tr>
<tr>
<td>In\textsubscript{40}Sb\textsubscript{60}</td>
<td>1050</td>
</tr>
<tr>
<td>In\textsubscript{50}Sb\textsubscript{50}</td>
<td>948</td>
</tr>
</tbody>
</table>
shown in Fig. 4 (a,b) and compared with the equilibrium phase diagrams. It can be seen that the minimum value of $T_{cr}$ corresponds to the stoichiometry of the In$_2$Bi and InSb compounds.

Therefore, in order to explain these data, it can be supposed that liquid alloys of these binary eutectic systems whose one component are InSb and In$_2$Bi chemical compounds, consist of two kinds of structural units: self-associated pure elements and chemically ordered InSb - In$_2$Bi-like atomic groups. The structure and composition changes with temperature are accompanied by concentration fluctuations which are most pronounced before the starting of crystallization.

In our previous studies the mole fraction of associates in liquid alloys of different concentration for an In-Bi system has been calculated using an association model [13]. As can be seen from Fig. 2 most of the associates exist over a wide temperature range for an In-Sb system, and they can be responsible for viscosity the temperature dependence, similar to the melts of the In-Bi system.

4. CONCLUSIONS

The viscosity temperature dependences for liquid In-Sb and In-Bi molten alloys showed anomalous behavior. An analysis of these dependences made it possible to conclude the existence of an inhomogeneous atomic distribution with InSb-In$_2$Sb- and In$_2$Bi- based structural units and self-associated microgroups of atoms. The changes of structure and composition were accompanied with concentration fluctuations in a liquid state before solidification.

REFERENCES