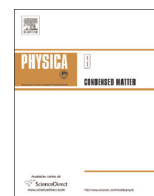




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Thermodynamic and structural properties of Bi-based liquid alloys

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ABSTRACT

Thermodynamic and microscopic structural properties of two Bi-based liquid alloys, such as In–Bi at 900 K and Tl–Bi at 750 K have been studied employing the regular associated solution model. We have estimated the mole fractions of the complexes and the free monomers assuming the existence of complexes In_2Bi in In–Bi melt and TlBi in Tl–Bi melt. The thermodynamic properties have been studied by computing the Gibbs free energy of mixing, enthalpy of mixing, entropy of mixing and activities of the monomers. The compositional contributions of the heat associated with the formation of complexes and the heat of mixing of the monomers to the net enthalpy change has also been studied. The structural properties of the liquid alloys have been studied by computing concentration fluctuation in the long-wavelength limit, chemical short-range order parameter and the ratio of mutual to intrinsic diffusion coefficients. For both of the alloy systems, the theoretical as well as the experimental values of $S_{\text{CC}}(0)$ are found to be lower than the corresponding ideal values over the whole composition range, indicating the hetero-coordinating nature of Bi–In and Bi–Tl alloy melts. All the interaction energy parameters are found to be negative and temperature dependent, and both the alloy systems are found to be weakly interacting.

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1. Introduction

It is well known that last twenty to twenty-five years a lot of world projects were dedicated to investigate lead free solders. Arising from the transition to Pb-free and the EU Reduction of Hazardous substances (RoHs) Directive, safety and environmental compliances issues exercise a dominant role and it was addressed aiming to develop new lead free alloys having equal characteristics or better than Sn–Pb solders widely used in the electronics industry. In Europe two COST projects (COST 531 and COST MP0602) were dedicated to study lead free alloys and for that purpose, a lot of work have been done. The alloys of bismuth (Bi) have low melting points. This feature makes the alloys of bismuth suitable for uses as solders and toxic solder containing lead can be replaced by safer bismuth [1–5]. Additionally, Pb is being replaced from its alloys by Bi in numerous applications, such as pigments for paints, fishing sinkers, bullets and shots, brass for plumbing and as ingredients in grease for lubrications for safety purposes. The Indium Bismuth (In–Bi) alloy is a crystalline solid which is used as a semiconductor and in photo-optic applications. It also possesses the superconducting properties [6]. These various uses have drawn the consent of most modern day researches to study and predict

the thermodynamic and structural behaviours of the Bi-based liquid alloys. Several theoretical models so far have been proposed to understand the complexities in thermodynamic and structural properties of the liquid alloys [7–18]. In this paper, the regular associated solution model [19–24] has been used to study and predict the thermodynamic and structural properties of two Bi-based liquid alloys, In–Bi at 900 K and Tl–Bi at 759 K.

According to the regular associated solution model, when atoms of types A and B are mixed in liquid state there is probability of associations among A, B; A, A and B, B. The regular solution can thus be regarded as the ternary mixtures of the complex (A–B) and the free monomers (A and B) and the three species are in equilibrium with each other. These associations are named as, 'complexes', 'pseudomolecules', 'clusters' or 'associations' [12]. It is also assumed that there exist unequal interactions among the associated and unassociated atoms. The expressions for different thermodynamic and structural functions are derived on this basis. Among the microscopic structural functions, the concentration fluctuation in long wavelength limit ($S_{\text{CC}}(0)$) has evolved as an important tool to predict the structure of the liquid alloys. Bhatia et al. [18] has shown that the concentration fluctuation in the long wavelength limit can be obtained from the model parameters even if the data from the low angle X-ray and neutron diffraction experiments are not available. The expressions for the $S_{\text{CC}}(0)$ and the thermodynamic functions of compound forming liquid binary alloys were derived by Bhatia and Hargrove [18]. However, the

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procedure of estimating the complex concentration and interaction energy parameters involves selection of initial values for the unknown parameters and spontaneous iteration to get the best fit values to explain the experimental data which is quite tedious. This procedure was significantly simplified by Lele and Ramchandrarao [21] which involves the estimation of the pairwise interaction energy parameters and the equilibrium constant from the activity coefficients of the components at infinite dilution and the activity data at one another intermediate compositions. The dependency of concentration fluctuation in long wave length limit ($S_{CC}(0)$) with the activity [14] and their relationship with the Gibbs free energy of mixing (G_M) can be understood in terms of the presence of the complexes. The phase diagram of In–Bi alloys [25] indicates the existence of different phases, such as β , "BiIn" (with tetragonal structure isotypic with PbO; δ , "BiIn₂" (with the hexagonal structure isotypic with InNi₂) and γ , "Bi₃In₅" (with the complex tetragonal structure isotypic with B₃Cr₅). Whereas, the phase diagram of Tl–Bi alloys [25] indicates the existence of phases, such as γ "Bi₃Tl₂" with a hexagonal structure and γ "Bi–Tl" with the fcc (Al) structure isotypic with Cu. Among these phases, this model well explains the thermodynamic and microscopic structural behaviours of the alloys considering the existence of In₂Bi complex in In–Bi and TlBi complex in Tl–Bi in the initial melts. We have thus estimated the stated behaviours assuming the existence of complexes In₂Bi in the In–Bi system and TlBi in the Tl–Bi system in the initial melts.

The expressions for the various thermodynamic and structural functions are presented in Section 2, the results and discussion is presented in Section 3 and the conclusion of this work is outlined in Section 4.

2. Theory

Let one mole of binary liquid solution contain n_1 atoms of monomer A (=In, Tl) and n_2 atoms of monomer B (=Bi) of the form A–B. According to Lele and Ramchandrarao [21], it is assumed that the chemical complexes $A_\mu B$ ($A_\mu B \rightleftharpoons \mu A + B$) exists in the melt, where μ is a small integer whose value is determined from the compound forming concentration ($=\mu/(\mu+1)$) in the solid state. The liquid mixture thus can be considered to be the ternary mixtures of free atoms A and B and the complex $A_\mu B$. Also let n_A , n_B and $n_{A_\mu B}$ moles are the respective concentrations of free atoms A, B and the complex $A_\mu B$ in the melt. Then according to the conservation of mass, in the partially associated solution the formation of the complex $A_\mu B$ requires $n_1 = n_A + \mu n_{A_\mu B}$ and $n_2 = n_B + n_{A_\mu B}$. But the thermodynamic and microscopic structural behaviours of the complexes in the melt are ruled by their true mole fractions x_A , x_B and $x_{A_\mu B}$ in spite of their gross mole fractions x_1 and x_2 , where $x_1 = n_1/n_1 + n_2$, $x_2 = n_2/n_1 + n_2$, $x_A = n_A/n_A + n_B + n_{A_\mu B}$, $x_B = n_B/n_A + n_B + n_{A_\mu B}$ and $x_{A_\mu B} = n_{A_\mu B}/n_A + n_B + n_{A_\mu B}$.

From the above expressions the equations for the true mole fractions can be derived as

$$x_A = x_1 - \mu x_2 x_{A_\mu B} \quad \text{and} \quad x_B = x_2 - (1 - \mu x_2) x_{A_\mu B} \quad (1)$$

According to the regular associated solution model, it is assumed that the gross chemical potentials of components 1 and 2 are equal to the chemical potentials of free monomers A and B [26]. According to Jordan [23], the activity coefficients of monomers γ_A , γ_B and complex $\gamma_{A_\mu B}$ can be represented in terms of pairwise interaction energies as

$$RT \ln \gamma_A = x_B^2 \omega_{12} + x_{A_\mu B}^2 \omega_{13} + x_B x_{A_\mu B} (\omega_{12} - \omega_{23} + \omega_{13}) \quad (2a)$$

$$RT \ln \gamma_B = x_{A_\mu B}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{A_\mu B} (\omega_{23} - \omega_{13} + \omega_{12}) \quad (2b)$$

$$RT \ln \gamma_{A_\mu B} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_A x_B (\omega_{13} - \omega_{12} + \omega_{23}) \quad (2c)$$

where ω_{12} , ω_{13} and ω_{23} represent the pairwise interaction energies for the species A, B; A, $A_\mu B$ and B, $A_\mu B$ respectively. T and R represent temperature and universal real gas constant respectively.

Following Lele and Ramchandrarao [21], the equilibrium constant for the reaction $A_\mu B \rightleftharpoons \mu A + B$ can be given by following equation:

$$k = \frac{x_A^\mu x_B \gamma_A^\mu \gamma_B}{x_{A_\mu B}^\mu \gamma_{A_\mu B}} \quad (3)$$

Solving Eqs. (2) and (3), the relation for the equilibrium constant can be obtained as

$$\ln k = \ln \left(\frac{x_A^\mu x_B}{x_{A_\mu B}^\mu} \right) + \frac{\omega_{12}}{RT} + \frac{\omega_{12}}{RT} [\mu x_B (1 - x_A) + x_A] + \frac{\omega_{13}}{RT} [\mu x_{A_\mu B} (1 - x_A) + x_A] + \frac{\omega_{23}}{RT} [x_{A_\mu B} (1 - \mu x_B) - x_B] \quad (4)$$

and the free energy of mixing (G_M) is given as [21]

$$G_M = \frac{1}{1 + \mu x_{A_\mu B}} RT \left[\left(x_A x_B \frac{\omega_{12}}{RT} + x_A x_{A_\mu B} \frac{\omega_{13}}{RT} + x_B x_{A_\mu B} \frac{\omega_{23}}{RT} \right) + (x_A \ln x_A + x_B \ln x_B + x_{A_\mu B} \ln x_{A_\mu B}) + x_{A_\mu B} \ln k \right] \quad (5)$$

The other thermodynamic functions, such as heat of mixing (H_M), entropy of mixing (S_M) and concentration fluctuation in the long wavelength limit ($S_{CC}(0)$) are related with free energy of mixing (G_M) by the following standard thermodynamic relations:

$$H_M = G_M - T \left(\frac{\partial G_M}{\partial T} \right)_P \quad (6a)$$

$$S_M = \frac{H_M - G_M}{T} \quad (6b)$$

$$S_{CC}(0) = RT \left(\frac{\partial^2 G_M}{\partial x_1^2} \right)_{T,P}^{-1} \quad (6c)$$

$$S_{CC}(0) = x_2 \alpha_1 \left(\frac{\partial \alpha_1}{\partial x_1} \right)_{T,P}^{-1} = x_1 \alpha_2 \left(\frac{\partial \alpha_2}{\partial x_2} \right)_{T,P}^{-1} \quad (6d)$$

Using Eq. (5) in Eq. (6a), the expression for the enthalpy of mixing can be obtained as

$$H_M = \frac{1}{1 + \mu x_{A_\mu B}} \left[\left(x_A x_B \frac{\omega_{12}}{RT} + x_A x_{A_\mu B} \frac{\omega_{13}}{RT} + x_B x_{A_\mu B} \frac{\omega_{23}}{RT} \right) - T \left(x_A x_B \frac{\partial \omega_{12}}{\partial T} + x_A x_{A_\mu B} \frac{\partial \omega_{13}}{\partial T} + x_B x_{A_\mu B} \frac{\partial \omega_{23}}{\partial T} \right) - x_{A_\mu B} RT^2 \frac{d \ln k}{dT} \right] \quad (7)$$

The expression for the concentration fluctuation in the long-wavelength limit ($S_{CC}(0)$) can be obtained by using Eq. (5) in Eqs. (6c) and (6d) as

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