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Correlation of bulk and surface properties in Bi-Sn and Bi- In liquid alloys

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ABSTRACT

We have used simple statistical model to report the energetic and its effect on the alloying behavior of Bi-Sn and Bi-In liquid alloys. The energetic of mixing in liquid alloys has been analyzed through the study of bulk and surface properties. In the bulk, we have studied thermodynamic properties, which include Gibb's free energy of mixing, enthalpy of mixing and entropy of mixing. The surface behavior has been analyzed by computing surface concentration and surface tension of the alloys. For the microscopic structural investigation our study includes concentration-concentration fluctuation in long wavelength limit and Warren-Cowley short range order parameter, they have been discussed in term of the energetic of the bulk as well as that of the surface part. The computed results are in good agreement with experimental data and support a weak phase-separation tendency in molten Bi-Sn system and ordering behavior in Bi-In system. In both system, temperature dependent energy parameter takes important role to explain bulk and surface properties. Copyright © 2015 VBRI Press.

Keywords: Surface properties; homo-coordinated alloys; thermodynamic properties; phase-separation.

Introduction

For the material preparation of metal alloys, the understanding of mixing properties of the liquid alloys is important. In order to understand a complete picture of mixing in binary liquid alloys it is necessary to know about the microscopic structure and the energetic of the bulk as well as surface phenomena. Both bulk and surface effects are being investigated separately by the application of various theoretical models **[1-9]**. Interactions among the constituent atoms of the alloys play an important role in the stability of liquid alloys. Besides bulk, theoretical studies of the surface phenomena are necessary for a better understanding and improvement on metallurgical processes and material design **[6]**. They are also essential for fundamental understanding of surface-related phenomena such as heterogeneous catalysis, epitaxial growth, corrosion, gas absorption, wetability at solder and weld joints, nucleation of gas bubbles, nucleation and growth of metallic inclusions **[10]**. The study in general leads to expression of knowledge in the field of material science and engineering for producing construction materials of enhanced properties such as increased material strength, heat and chemical resistance, radiation resistance, a wider range of colour not found naturally and even economic from point of view of production cost **[10]**.

Here an attempt has been made to correlate the bulk phenomenon of Bi-Sn and Bi-In liquid alloys with its surface properties through the study of the concentration dependence of various thermodynamic and structural properties. The grand partition function for the system has been solved under the frame work of simple statistical model to obtain analytical expressions for various parameters **[11]**. Surface segregation has been discussed in terms of the energetic of the bulk as well as that of the surface part. The presented model is the very simple model which pronounces the alloys system either homo-coordination or hetero-coordination. The model with single energy parameter, i.e. interchange or ordering energy successfully explains the mixing behaviors of the liquid alloys. The theoretical formalism for the bulk thermodynamic functions are presented which deals with microscopic structural function while surface properties are presented.

Theoretical formalism

Bulk thermodynamic properties

Bulk Gibb's free energy of mixing, G_M:

The bulk grand partition function for simple binary liquid alloys AB which consists of N_A (=N x) number of A atoms and N_B (=N (1-x)) number of B atoms so that total number atoms N, becomes equal to N_A+N_B, may be expressed as **[11, 12]**.

$$\Xi^{b} = [\phi_A q_A(T)]^{N_A}\ [\phi_B q_B(T)]^{N_B} \exp(-\beta E), \qquad \beta = 1/k_B T \qquad (1)$$

where $q_i^{N_i}$ are the partition functions of atoms (i =A or B) associated with inner and vibrational degree of freedom. q_i the same whether the atom i is located in the pure state or in alloy. $\phi_i\ (i = A \text{ or } B)$ is given as

$$\phi_i = \exp(\mu_i / k_B T), \qquad (2)$$

where μ_i, k_B and T refer to chemical potential of ith component, Boltzmann constant and absolute temperature, respectively. E is the configurational energy of the alloys. One can easily obtain a relation between excess free energy of mixing, G_M^{XS} and the ratio of activity coefficients, γ (= γ_A / γ_B) by using standard thermodynamic relations **[12]**.

$$G_M^{XS} = RT\int_0^x \ln\gamma\, dx = RT[x\ln\gamma_A + (1-x)\ln\gamma_B] \quad (3)$$

$$\text{With} \quad \gamma_A = [(\beta - 1 + 2x)/x(1+\beta)]^{z/2} \qquad (3a)$$

$$\gamma_B = [(\beta + 1 - 2x)/(1-x)(1+\beta)]^{z/2} \qquad (3b)$$

$$\beta = \{1 + 4x(1-x)[\exp(2\omega/zk_B T) - 1]\}^{1/2} \qquad (3c)$$

where, R is universal molar constant; x is concentration of the component; ω is interchange or ordering energy and z is coordination number. The standard thermodynamic relation for Gibb's free energy of mixing (G_M) is

$$G_M = RT[x\ln x + (1-x)\ln(1-x)] + G_M^{XS} \qquad (4)$$

Using the relations **(3)** and **(4)**, one obtains an expression for the Gibb's free energy of mixing **[10, 12]** as

$$\begin{aligned} G_M &= RT[x\ln x + (1-x)\ln(1-x) + x\ln\gamma_A + (1-x)\ln\gamma_B] \\ &= RT[x\ln x + (1-x)\ln(1-x) + x(1-x)\frac{\omega}{k_B T}] \end{aligned} \qquad (5)$$

Enthalpy of mixing, H_M and entropy of mixing, S_M

The calculation of enthalpy and entropy of mixing are of immense relevance since they will likely to provide information on the temperature dependence of the ordering energy. The enthalpy of mixing (H_M) can be obtained from the standard thermodynamic expression

as

$$\begin{aligned} H_M &= G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{x,P,N} \\ &= RT\left[x(1-x)\frac{\omega}{k_B T} - x(1-x)\frac{1}{k_B}\frac{d\omega}{dT}\right] \end{aligned} \qquad (6)$$

And entropy of mixing (S_M) can be worked out from the relation

$$S_M = (H_M - G_M)/T \qquad (7)$$

Bulk structural properties

Bulk concentration-concentration fluctuations in the long wavelength limit, $S_{cc}^{b}(0)$:

$S_{cc}^{b}(0)$ is an essential structural function which has been widely used to study the nature of atomic order in binary liquid alloys[13]. It is thermodynamically related to Gibb's free energy of mixing (G_M) through the equation

$$S_{cc}^{b}(0) = RT\left(\frac{\partial^2 G_M}{\partial x^2}\right)_{T,P,N}^{-1} \qquad (8)$$

Equations **(5)** and **(8)** gives the theoretical value of $S_{cc}(0)$:

$$S_{cc}^{b}(0) = x(1-x)[1 + z(1-\beta)/2\beta]^{-1} \qquad (9)$$

For the ideal mixing, when the ordering energy is zero, concentration-concentration fluctuations are usually computed from:

$$S_{cc}^{b}(0, id) = x(1-x) \qquad (10)$$

Bulk Warren-Cowley short range order parameter, α_1

The Warren-Cowley **[14, 15]** short-range order parameter (α_1) is another important structural function which is useful to quantify the degree of chemical order in the alloy at melt. It provides insight into the local arrangement of the atoms in the molten alloys. Although it is difficult to obtain the experimental values of α_1, theoretical values of this parameter are easily obtain via conditional probability [A/B] which defines the probability of finding an A- atom as a nearest neighbor of a given B-atom. It can be evaluated theoretically **[14, 15]:**

$$\alpha_1 = (S-1)/\{S(z-1)+1\}, \qquad S = S_{cc}(0)/S_{cc}^{id}(0) \qquad (11)$$

where z is the coordination number, which is taken as 10 for our purposes.

Surface properties

Surface concentration and surface tension: The knowledge of surface phenomena i.e. surface segregation and surface tension of the alloys can help to explain the technological important various properties such as mechanical behavior, kinetics of phase transformation, catalytic activity of alloy catalyst and thin film etc. Surface segregation is the enrichment of the surface by the atoms of the particular component element in a binary alloy which results from the interaction among the atoms and surface tension **[3]**. Binary liquid alloy is considered to have a layered structure near the surface with thermodynamic equilibrium existing between the species at the surface and in the bulk **[4]**. The surface properties of liquid alloys are influenced by their bulk thermodynamic properties. The surface grand partition function is related to the surface tension τ by the expression **[3, 4]**

$$\Xi^{s} = \exp\left(\frac{-S\tau}{k_B T}\right) = \exp\left(\frac{-N^{s}\tau\xi}{k_B T}\right) \qquad (12)$$

where S is the surface area and ξ is the mean area of the surface per atom and is defined as $\xi = S/N^s$,and N^s is the total number of atoms at the surface. k_B is the Boltzmann constant.

A pair of equation for surface tension of the binary liquid alloys in terms of activity coefficient (γ_i) of the alloy components and interchange energy parameter (ω), at the given temperature T, proposed by Prasad et al, have been modified in the simple form, using zeroth approximation**[13]** as

$$\tau = \tau_A + \frac{k_B T}{\xi}\ln x^s - \frac{k_B T}{\xi}\ln x + \{p(1-x^s)^2 + (q-1)(1-x)^2\}\frac{\omega}{\xi} \qquad (13a)$$

$$\tau = \tau_B + \frac{k_B T}{\xi}\ln(1-x^s) - \frac{k_B T}{\xi}\ln(1-x) + \{p(x^s)^2 + (q-1)x^2\}\frac{\omega}{\xi} \qquad (13b)$$

where τ_A and τ_B are the surface tension values for the pure components A and B respectively; x and x^s are the bulk and surface concentrations of the alloy component; p and q are the surface coordination fractions, which are defined as the fraction of the total number of nearest neighbors made by atom within its own layer and that in the adjoining layer. For p and q, the following relation is available **[4].**

$$P + 2q = 1 \qquad (14)$$

For closed packed structure, p = 0.5 while q = 0.25(in view of the disordered structure and relaxation effect of the surface layer p and q should be treated as parameters [3]). The pair of **Eqs.17(a)** and **17(b)** can be solved numerically to obtain x^s as a function of x. Obviously the surface concentration depends upon the surface tension of the ith component in the pure state(τ_i) , surface area per atom(ξ), order energy(ω) and the coordination fractions(p and q). This approach is useful because it can be used to investigate the dependence of surface composition on order energy and surface coordination.

The mean atomic surface area ξ (=A/N^s) is given as

$$\xi = \sum c_i \xi_i \qquad (i = A, B) \qquad (15)$$

Where the atomic area of hypothetical surface for each component is given as **[3,4]:**

$$\xi_i = 1.102\left(\Omega_i / N_0\right)^{2/3} \qquad (16)$$

where Ω_i is the molar volume of the species i and N_0 stands for Avogadro number.

Surface concentration-concentration fluctuations in the long wavelength limit and Warren-Cowley short range order parameter

In order to compare the behavior of concentration-concentration fluctuations and Warren-Cowley short rang order parameter in the bulk and at the surface of the alloys, we need an expression for determination of concentration-concentration fluctuations and warren-Cowley short rang order parameter at the surface. On the basis of earlier works of Singh et al. in ref.**[12]** for the bulk phase, an expression for concentration- concentration fluctuations at the surface obtained via solving the surface grand partition function is given by[1]

$$S^s_{cc}(0) = x^s(1-x^s)[1 + z^s(1-\beta^s)/2\beta^s]^{-1} \qquad (17)$$

$$\beta^s = \left\{1 + 4x^s(1-x^s)\left[\exp(2\omega/z^s k_B T) - 1\right]\right\}^{1/2} \qquad (18)$$

Here z^s is the coordination number of surface atoms which is obtained from z^s = (p+q) z and z is the coordination number in bulk. In the case of ideal mixing (i.e. ω = 0), **Eq.(21)** reduces to

$$S^s_{cc}(0, \text{ideal}) = x^s(1-x^s) \qquad (19)$$

The expression for the surface Warren-Cowley short range order parameter, deduced from Eq.(11) is given by

$$\alpha_1^s = (S^s - 1)/\{S^s\,(z^s - 1) + 1\}, \quad S^s = S^s_{cc}(0)/x^s(1-x^s) \qquad (20)$$

Results and discussion

In general the mixing properties of binary metal alloys vary as a function of composition, temperature and pressure. As the study of the liquid alloys is usually carried out at the fixed pressure, most likely the atmosphere pressure, the thermo-physical properties of a binary liquid alloys at the given temperature vary with composition of the alloys. In the present work, we have studied the composition dependence of the bulk thermodynamic, structural and surface properties of Bi-Sn and Bi-In alloys at constant temperatures 600K and 900K respectively. It is understood from the theory that there are some parameters that need to be fitted in order to carry out the present calculations. The parameters are the coordination number (z), interchange energy (ω) and temperature derivative of interchange energy (dω/dT). For uniformity, the coordination number (z) in the liquid phase was chosen as 10. We observed that the choice of z does not significantly affect our results.

Interchange energy (ω) and temperature derivative of interchange energy (dω/dT) for both alloys system have been estimated by the method of successive approximation using experimental data of free energy of mixing(G_M) and enthalpy of mixing(H_M) over the whole range of concentration**[17]**. Once suitable values of these parameters are chosen, the theory allows to calculate other quantities mentioned above. The values of the fitted parameters for the two alloys system are presented in **Table 1**.

Table 1. Basic parameters.

Alloys	T(K)	z	ω (ev)*	dω/dT(ev/K)*
Bi-Sn	600	10	+0.0108675	$+1.08675\times10^{-5}$
Bi-In	900	10	-0.0797208	-4.14000×10^{-6}

*The values of these parameters are obtained by thermodynamic fitting.

Bulk thermodynamic properties

Eqs. (5), (6) and **(7)** have been used to compute G_M/RT, H_M/RT and S_M/ R. **Fig. 1, 2** and **3** show the result of these computations. We observed that there are remarkable agreement between computed and their respective experimental data **[17]**.

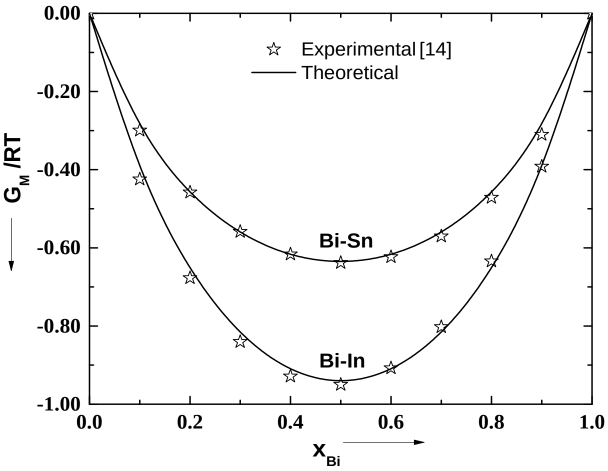

Fig. 1. Free energy of mixing (GM) Vs bulk concentration of Bismuth (xBi) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. Solid line for theoretical values and stars for Experimental data **[14].**

The implication of ω in the **Table 1** being positive for the Bi-Sn and negative for the Bi-In system is that former is segregating and latter is chemically ordered. Small values of ω suggest that they are weakly interacting. The remarkable agreement between computed G_M/RT and their respective experimental data **(Fig. 1)** confirms that the choice of ω for the two alloys is quite reasonable. The plots **(Figs. 2** and **Fig. 3)** resulting from **Eqs.(6)** and **(7)** which incorporated temperature dependence of interchange energy(dω/dT) shows a remarkable agreement between the experimental data and the computed values which confirms the temperature dependence of the interchange energy of the two alloys. The results of enthalpy of mixing H_M/RT for Bi-Sn and Bi-In are shown in **Fig. 2** respectively compared with experimental results **[17].** The positive value indicates presence of homo-coordination in that concentration range as the case for Bi-Sn, while both the experimental and computed values for Bi-In show negative trend indicating clustering of unlike atoms or hetero-coordination. The results for the entropy of mixing for Bi-Sn and Bi-In are also plotted with concentration in **Fig. 3.** The positive value of S_M/R shows the presence of atomic order. More positive values of S_M/R within entire concentration confirms that Bi-In system is hetero-coordinated alloys. The computed value of the entropy of mixing (S_M/R) for Bi-Sn and Bi-In systems are also compared with experimental results. We observed that there are also remarkable agreement between computed and their respective experimental data.

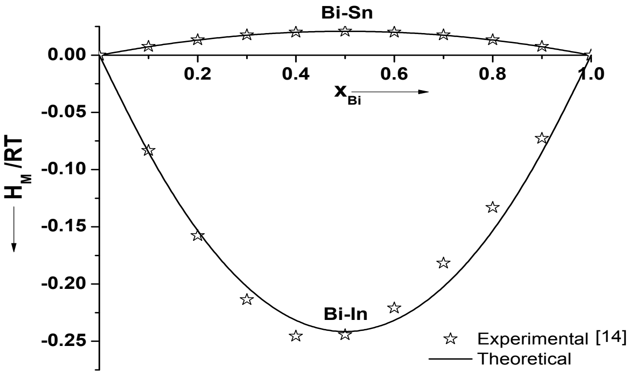

Fig. 2. Heat of mixing (HM) Vs bulk concentration of Bismuth (xBi) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. Solid line for theoretical values and stars for Experimental data **[14].**

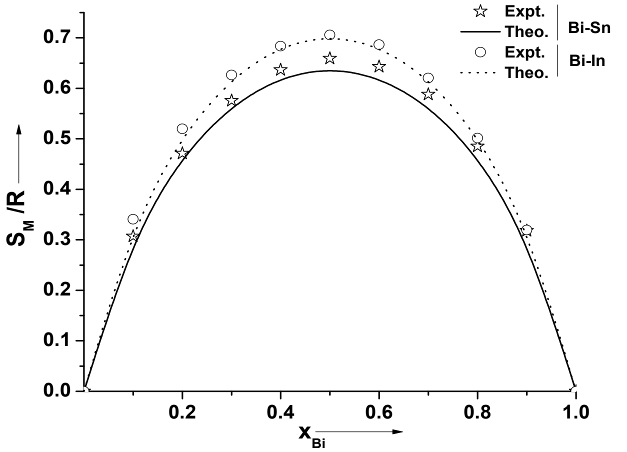

Fig. 3. Entropy of mixing (S_M) Vs bulk concentration of Bismuth (x_{Bi}) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. For Bi-Sn, solid line for theoretical values and stars for Experimental data **[14]**.For Bi-In, dotted line for theoretical values and stars for Experimental data **[14].**

Bulk structural properties

To understand the nature, strength and level of influence of the order in the properties of the alloys, we consider the calculated bulk concentration-concentration fluctuations and Warren-Cowley chemical short range order parameter using the energy parameter obtained from earlier calculations. The bulk concentration-concentration fluctuations ($S^b_{cc}(0)$) and the Warren-Cowley chemical short range order parameter (α^b_1) have been computed via. **Eqs. (9)** and **(11).** We have used **Eq. (9)** to compute the $S_{cc}(0)$ theoretically for both alloys. It can also be obtained directly from the measured activity **[14]** data as

$$S_{cc}(0) = (1-x)a_A\left(\frac{\partial a_A}{\partial x}\right)^{-1} = xa_B\left(\frac{\partial a_B}{\partial(1-x)}\right)^{-1} \qquad (21)$$

where a_A and a_B are the observed chemical activities of constituents of the alloys. The $S_{cc}(0)$, obtained from **Eq. (21)** are taken as experimental values. **Fig. 4** shows a plot of the computed and experimental values of $S_{cc}^{b}(0)$ along with the ideal values. The computed values of $S_{cc}^{b}(0)$ are in good agreement with the experimental values of $S_{cc}^{b}(0)$ for both alloys. The result can be used to understand the nature of atomic order in binary liquid alloys. At a given composition if $S_{cc}(0) < S_{cc}^{id}(0)$, ordering in liquid alloy is expected while $S_{cc}(0) > S_{cc}^{id}(0)$ gives the indication of tendency of segregation. $S_{cc}^{id}(0)$ is the ideal value of $S_{cc}(0)$ which is associated with alloys of ideal mixture. In **Fig. 4**, it is seen that for Bi-Sn system $S_{cc}^{b}(0) > S_{cc}^{b}(0, id)$ but for Bi-In system $S_{cc}^{b}(0) < S_{cc}^{b}(0, id)$ which show that liquid Bi-Sn alloys at 600K is of homo-coordinating in nature whereas liquid Bi-In alloys at 900K is of hetero-coordinating nature.

In addition, Warren-Cowley CSRO parameter (α_1) provides an immediate insight into the nature of the local arrangement of atoms in the mixture. The minimum possible value of α_1 is -1 and it indicates complete ordering of unlike atom pairing at nearest atoms. On the other hand the maximum value of α_1 is +1, which implies complete segregation leading to phase separation and $\alpha_1 = 0$ corresponds to a random distribution of atoms. **Fig. 5** shows the plots of α_1^b against chemical composition, obtained from **Eq. (11).** In the Bi-Sn system, α_1^b is found positive throughout concentration of Bi but it is negative throughout same concentration of Bi in the Bi-In system. The positive values of α_1^b throughout whole concentration range of Bi **(Fig. 5)** is the signatures of segregating in the Bi-Sn liquid alloys at 600K but negative values of α_1^b is the confirmation of chemical ordering in the Bi-In liquid alloys at 900K.

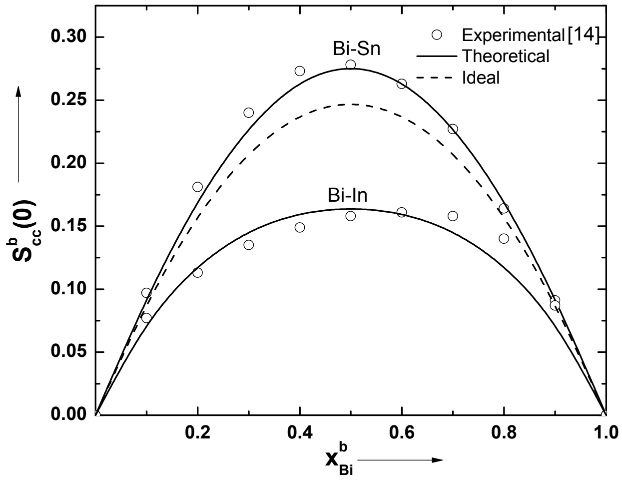

Fig. 4. Bulk concentration fluctuation at long wavelength limit ($S_{cc}^{b}(0)$). Vs bulk concentration of Bismuth (x_{Bi}^{b}) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. Solid line for theoretical values and circles for Experimental data **[14]**. Dashed line represents the ideal values of concentration fluctuation, $S_{cc}(0,id)$.

Surface properties

The surface concentrations and surface tension of the alloys Bi-Sn and Bi-In have been computed numerically from the **Eqs. 13(a)** and **13(b).** For this, we need experimental data of density and surface tension of the components at the working temperature.

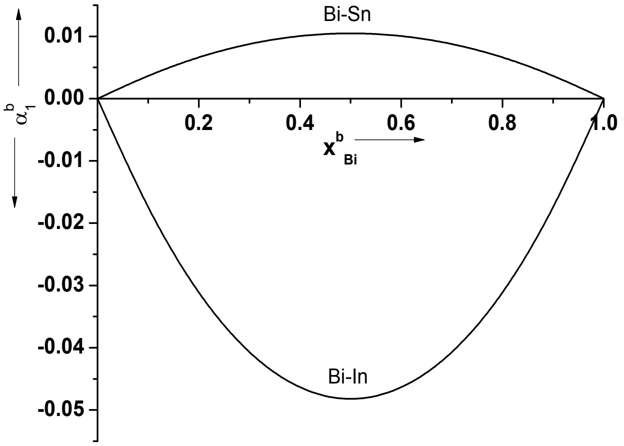

Fig. 5. Bulk chemical short range order parameter (α_1^b) Vs bulk concentration of Bismuth (x_{Bi}^b) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively.

The density and surface tension for the components of the alloys **[18, 19]** at the respective working temperature T have been calculated by using the following equations and values given in **Table 2**.

$$\rho(T) = \rho_0 + (T - T_0)\frac{d\rho}{dT} \qquad (22)$$

$$\tau(T) = \tau_0 + (T - T_0)\frac{d\tau}{dT} \qquad (23)$$

Where T and T_0 are respectively working temperature and melting temperature; $\frac{d\rho}{dT}$ and $\frac{d\tau}{dT}$ represent the temperature coefficient of density and surface tension respectively for component metal of the alloys. The mean atomic surface area ξ has been calculated by using **Eqs. (15)** and **(16).** For calculating surface tension we used same estimated energy parameter, ω. At first, surface concentrations of the component in alloy have been obtained as a function of bulk concentration by concurrently solving the equations **13(a)** and **13(b).** Using the obtained values of surface concentrations we computed the surface tension of liquid alloys at working temperature for whole concentration range.

Table 2. Essential parameters for the surface property calculations.*

Atom	**T_0 (^{0}C)**	**ρ_0 ($\times 10^{3}$ kg/m^3)**	**τ_o ($\times 10^{-3}$N/m)**	**dρ/dT (kg/m^{3}K)**	**dτ/dT ($\times 10^{-3}$ N/mK)**
Bi	271	10.068	378	-1.3300	-0.07
Sn	232	7.000	544	-0.6127	-0.07
In	156.6	7.023	556	-0.6798	-0.09

*The values of these parameters are obtained from **[15, 16].**

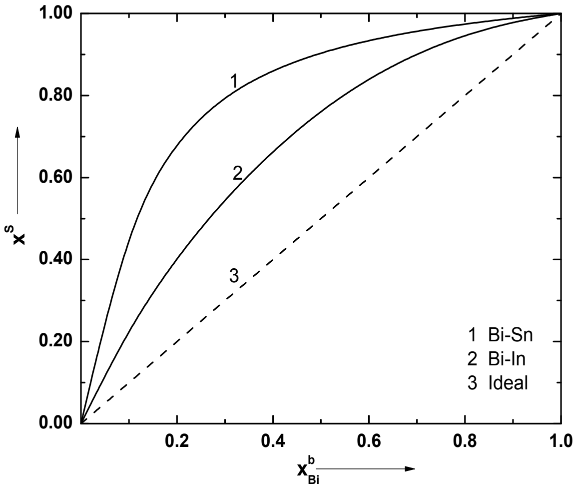

Fig. 6. Surface concentration (x^s) Vs bulk concentration of Bismuth (x^b_{Bi}) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. 1 for Bi-Sn, 2 for Bi-In and 3 for ideal values.

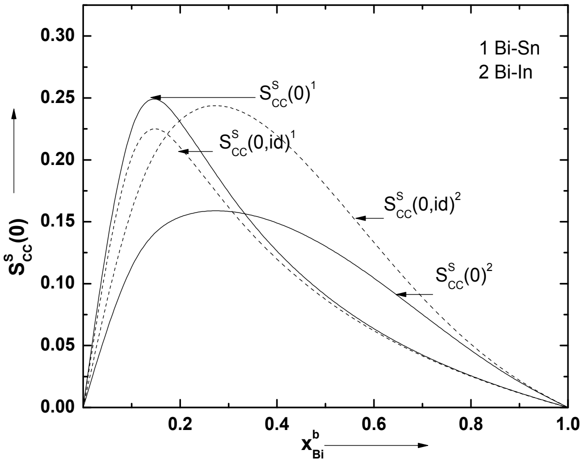

Fig. 8. Surface concentration fluctuation at long wavelength limit ($S^S_{CC}(0)$) Vs bulk concentration of Bismuth (x^b_{Bi}) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. Dotted line represents ideal values for surface concentration fluctuation ($S^S_{CC}(0, id)$).

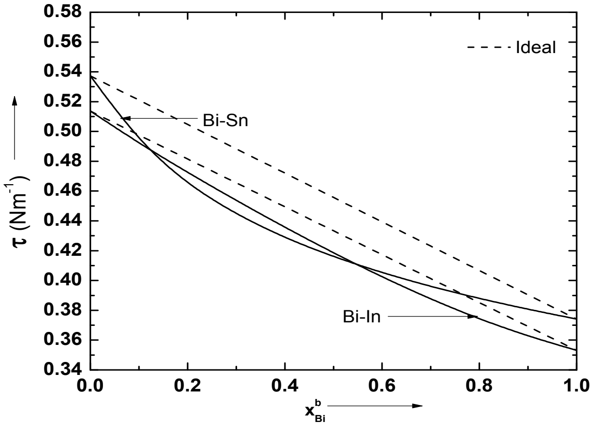

Fig. 7. Surface tension (τ) Vs bulk concentration of Bismuth (x^b_{Bi}) for Bi-Sn and Bi-In liquid alloys at 600K and 900K respectively. Dotted line represents ideal values.

The study of surface concentration as shown in **Fig. 6** shows the usual pattern for surface concentration increasing with increasing bulk compositions. This indicates that Bi-atoms (having lower value of surface tension relative to Sn-atoms and In-atoms) segregate respectively at the surfaces of liquid alloys Bi-Sn and Bi-In in preference to Sn-and In-atoms throughout the entire compositions. The high degree of segregations of Bi-atoms on the respective surfaces of Bi-Sn and Bi-In systems (as signaled by the large deviations between their computed surface concentration plots and ideal plot) is a confirmation of the presence of CSRO at the surfaces of the two systems and the contribution of CSRO to the segregation of Bi-atoms on the respective surfaces of Bi-Sn and Bi-In systems is quite significant.

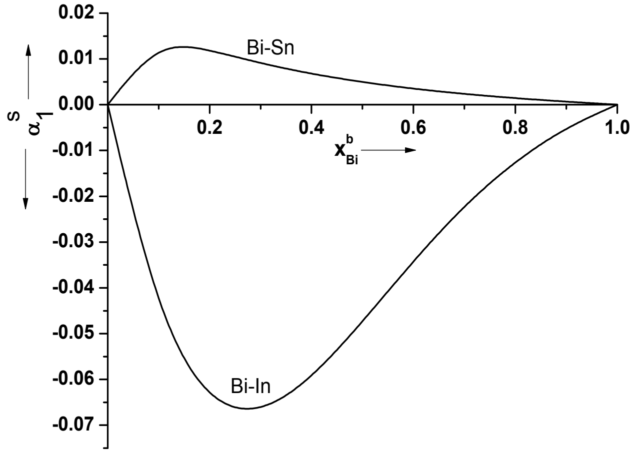

Fig. 9. Surface chemical short range order parameter (α^S_1) Vs bulk concentration of Bismuth (x^b_{Bi}) in liquid Bi-Sn alloy at 600K and in liquid Bi-In alloy at 900K.

The computed values of surface tension for molten alloys Bi-Sn and Bi-In respectively at 600 and 900K from modified Prasad's model, mentioned above are depicted in **Fig. 7**. Due to lack of surface tension experimental data we could not compare our computed surface tension with the experimental data, nonetheless, we observed that the isothermal plots of surface tension of the systems exhibit negative deviation from the ideal values ($\tau = \tau_A x + \tau_B(1-x)$) as it is the case with most binary liquid mixtures **[14]**. It is noticed that computed values of τ of the two alloys systems are found smaller than the ideal values throughout bulk concentration of bismuth. More negative deviation of Bi-Sn system from their ideality is observed as compared to Bi-In system **(Fig. 7).** To predict the local order on the surface of the liquid alloys, the surface concentration- concentration fluctuations, $S^S_{CC}(0)$ and surface warren-Cowley short range order parameter, α^S_1 was computed through **eq. (17)** and **(20)** and plotted against the bulk concentrations of bismuth of the alloys Bi-Sn and Bi-In in **Fig. 8** and **9**. The **Fig. 8** shows that $S^S_{CC}(0)$ and $S^S_{CC}(0, id)$ for the alloys are skewed towards the lower concentrations of bismuth. However just as in fig.4, fig. 8 shows $S^s_{cc}(0) < S^s_{cc}(0, id)$ throughout the entire composition of bismuth in Bi-In and $S^s_{cc}(0) > S^s_{cc}(0, id)$ in the Bi-Sn system, in which former indicates the presence of chemical order and latter shows segregating nature both in bulk and on the surface of the liquid alloys.

Conclusion

Our analysis reveals that the system Bi-Sn and Bi-In respectively at 600K and 900K are homo-coordinated and hetero-coordinated in the bulk and surface throughout the entire composition of bismuth. Thermodynamic properties and structural functions are deviated positively from their ideality in the former case but in the later case they are found to deviate negatively. The theoretical analysis suggests that both alloys are of weakly interacting nature. Surface tension isotherms of both alloys are deviated negatively from their ideal values. Theoretical study proofs that metal with lower surface tension tends to segregate on the surface of molten alloys. The bigger Bi-atoms segregate at surface in the both case of liquid alloys. Smaller Sn-atoms segregate in the bulk, in the case of liquid Bi-Sn alloys whereas in case of liquid Bi-In alloys segregation of In-atoms occurs.

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