Thermodynamic and surface properties of Sb–Sn and In–Sn liquid alloys

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Abstract. The thermodynamic properties of Sb–Sn and In–Sn liquid alloys have been studied using the quasi-chemical model for compound forming binary alloys and that for simple regular alloys. The concentration fluctuation $S_{cc}(0)$ and the Warren–Cowley short-range order parameter (α_1) were determined for the whole concentration range at a temperature of 770 K. The surface tensions of these liquid alloys were determined for the whole concentration range by using energetics determined from thermodynamic calculations. In all calculations, In–Sn manifested properties very close to alloys of ideal mixing, while Sb–Sn showed properties that are asymmetric about equiatomic composition. Our results suggest that a weak complex of the form $SbSn_2$ could be present in the Sb–Sn alloy at a temperature of about 770 K.

Keywords. Liquid alloys; surface properties; concentration fluctuation.

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1. Introduction

Alloys of Sn are likely to be very promising as an alternative solder in the electronic industry [1–3]. This is because the commonly used solder consists of lead which is known to be toxic to the human body and causes serious environmental problems [4,5]. To develop a lead-free solder, a good knowledge of surface properties such as interfacial adhesion and surface tension is necessary. This is because these properties are known to play an important role in the wettability and production of acceptable solder joints [6,7].

In this study, the thermodynamic properties of two tin-based alloys, Sb–Sn and In–Sn, are studied with the aim of determining and understanding from a theoretical point of view the properties of the liquid alloys in the bulk and at the surface. To carry out this study, the quasi-chemical formulation [8] which has proved successful in the study of thermodynamic properties and ordering in compound forming liquid alloys will be used to estimate the thermodynamic properties of the alloy throughout

the concentration range. This formulation in addition to suggesting a probable complex which may be predominant in the alloy will also indicate the possible strength of the complex.

To study the surface properties, the statistical formulation of Prasad *et al* [9] based on the concept of layered structure near the interface is used. This formulation links surface properties of a liquid binary alloy to its bulk thermodynamic properties through the activity coefficients of the alloy components in the bulk. Consequently, it will be possible to study the effect of observed bulk thermodynamic behaviour on the surface properties of the liquid binary alloy thus making it possible to make deductions about the surface based on observed bulk thermodynamic properties of the alloy.

In the next section, the basic expressions for the formulations used in this calculation are presented. Section 3 gives the results and discussions of this work and the conclusions are outlined in §4.

2. Theoretical concepts

The quasi-chemical formulation is used to determine the possible chemical complexes existing in a liquid binary alloy. The fundamental idea about the quasi-chemical model is that the thermodynamic properties of a compound forming A–B alloy can be explained by treating the alloy as a pseudoternary mixture of A atoms, B atoms and $A_\mu B_\nu$ complexes. Details of the formulations are given in ref. [8]

The excess free energy of mixing G_m^{es} is related to the free energy G_m by the expression

$$G_m^{es} = G_m - RT[x \ln x + (1-x) \ln(1-x)]. \tag{1}$$

Here, x is the concentration of atom A and R is the universal gas constant. The quasi-chemical expression for the excess free energy of mixing G_m^{es} is given as

$$\frac{G_m^{es}}{RT} = z \int_0^x [\ln \sigma + (2kT)^{-1}(P_{aa}\Delta\epsilon_{aa} - P_{bb}\Delta\epsilon_{bb})]\mathrm{d}x + \psi, \tag{2}$$

where z is the coordination number, k is the Boltzmann constant and

$$\ln \sigma = \frac{1}{2} \ln \frac{(1-x)(\beta + 2x - 1)}{x(\beta - 2x + 1)} \tag{3}$$

with

$$\beta = [1 + 4x(1-x)(\eta^2 - 1)]^{1/2} \tag{4}$$

and

$$\eta^2 = \exp\left(\frac{2w}{zkT}\right) \exp\left(\frac{2P_{ab}\Delta\epsilon_{ab} - P_{aa}\Delta\epsilon_{aa} - P_{bb}\Delta\epsilon_{bb}}{kT}\right). \tag{5}$$

w, $\Delta\epsilon_{ab}$, $\Delta\epsilon_{aa}$ and $\Delta\epsilon_{bb}$ are the interaction parameters with w denoting the interchange energy and $\Delta\epsilon_{ij}$ being the change in the energy if the ij bond is in the

complex $A_\mu B_\nu$. P_{ij} denotes the probability that the bond is part of the complex and the expressions are given as follows:

$$P_{ab} = x^{\mu-1}(1-x)^{\nu-1}[2 - x^{\mu-1}(1-x)^{\nu-1}], \tag{6}$$

$$P_{aa} = x^{\mu-2}(1-x)^{\nu}[2 - x^{\mu-2}(1-x)^{\nu}], \quad \mu \geq 2, \tag{7}$$

$$P_{bb} = x^{\mu}(1-x)^{\nu-2}[2 - x^{\mu}(1-x)^{\nu-2}], \quad \nu \geq 2. \tag{8}$$

The constant ψ is determined from the requirement that $G_{\mathrm{m}} = 0$ at $x = 1$.

For simple regular alloys, the quasi-chemical expression reduces to a one-parameter model and the excess free energy of mixing is now given as [10]

$$G_{\mathrm{m}}^{\mathrm{es}} = RT[x \ln \gamma_A + (1-x) \ln \gamma_B], \tag{9}$$

where γ_A and γ_B are the activity coefficients of the A and B atoms of the A–B alloy respectively and are given by the expressions

$$\gamma_A = \left\{ \frac{\beta - 1 + 2x}{x(1+\beta)} \right\}^{(1/2)z}, \tag{10}$$

$$\gamma_B = \left\{ \frac{\beta + 1 - 2x}{(1-x)(1+\beta)} \right\}^{(1/2)z} \tag{11}$$

with β already given in eq. (4). However for a simple regular alloy, η is given by

$$\eta = \exp(w/zkT). \tag{12}$$

The activities of the metals are obtained by

$$a_i = x\gamma_i, \tag{13}$$

where x is the concentration of the species and γ_i are their respective activity coefficients already given in eqs (10) and (11).

The concentration–concentration fluctuations in the long wavelength limit $S_{\mathrm{cc}}(0)$ for the compound forming liquid alloys has been shown to be given by

$$S_{\mathrm{cc}}(0) = x(1-x) \left\{ 1 + \frac{1}{2}z \left(\frac{1}{\beta} - 1 \right) + \Omega \right\}^{-1}, \tag{14}$$

where Ω is the expression given below:

$$\Omega = \frac{zx(1-x)}{2\beta kT} \Theta \tag{15}$$

and

$$\Theta = [2(1-2x)P'_{ab}\Delta\epsilon_{ab} + (\beta - 1 + 2x)P'_{aa}\Delta\epsilon_{aa} - (\beta + 1 - 2x)P'_{bb}\Delta\epsilon_{bb}],$$

(16)

where the prime on P denotes the first derivative with respect to x. However for the simple regular alloys, the $S_{cc}(0)$ is given as

$$S_{cc}(0) = \frac{x(1-x)}{1 + \frac{1}{2}z(1-\beta)/\beta}.$$

(17)

The Warren–Cowley [11,12] short-range order parameter α_1 for the first nearest neighbours is expressed as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1}.$$

(18)

In the model for studying surface properties, a statistical mechanical approach which derives from the concept of a layered structure near the interface was used by Prasad *et al* [9] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension ζ by the expression

$$\Xi^s = \exp\left(\frac{-A\zeta}{kT}\right) = \exp\left(\frac{-N^s\zeta\xi}{kT}\right),$$

(19)

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

Prasad *et al* [9] gave the expression for surface tension of the binary alloys in terms of activity coefficient of the alloy components as

$$\zeta = \zeta_A + \frac{kT}{\xi}\ln\frac{x_A^s}{x_A} - \frac{kT}{\xi}\ln\gamma_A + [p(x_B^s)^2 + q(x_B)^2]\frac{w}{\xi},$$

(20)

$$\zeta = \zeta_B + \frac{kT}{\xi}\ln\frac{x_B^s}{x_B} - \frac{kT}{\xi}\ln\gamma_B + [p(x_A^s)^2 + q(x_A)^2]\frac{w}{\xi},$$

(21)

where ζ_A and ζ_B are surface tension values for the pure components A and B respectively. x_i and x_i^s are the bulk and surface concentrations of the alloy components respectively. γ_A and γ_B are the bulk activity coefficients of the alloy components, w is the interchange energy and p and q are the surface coordination fractions.

The surface $S_{cc}(0)$ can be written as [9]

$$S_{cc}^s(0) = x_A^s x_B^s \left[1 + \left(\frac{z^s}{2\beta^s}\right)(1 - \beta^s)\right]^{-1},$$

(22)

where

$$\beta^s = \left\{1 + 4x_A^s x_B^s \left[\exp\left(\frac{2w}{z^s kT}\right) - 1\right]\right\}^{1/2}.$$

(23)

Here, z^s is the coordination number of the surface atoms which is obtained from $z^s = (p+q)z$ and z is the coordination number in the bulk.

3. Results and discussion

In this study, the thermodynamic model of Singh [8] for compound forming liquid binary alloys was used to reproduce the measured activity and free energy of mixing for Sb–Sn liquid alloys. In the case of In–Sn, the quasi-chemical formulation for simple regular binary alloys was used. In each case, the energetics obtained were used to compute the concentration fluctuation at the long wavelength limit $S_{\text{cc}}(0)$ and the Warren–Cowley short-range order parameter (α_1). These quantities are important from the point of view of understanding the extent of local order in the bulk of liquid binary alloys. Further, the surface properties are estimated using the calculated thermodynamic quantities such as the activity coefficients.

In the phase diagram for Sb–Sn [13,14], there are no indications of possible compounds or complexes formed in the liquid state. The quasi-chemical formulation for simple regular alloys proved inadequate in reproducing the measured thermodynamic properties of this alloy. This suggests that the order in this alloy is not simple and hence some form of complex activity may be present in some measure in this alloy. Below the liquidus line of the Sb–Sn alloy exists the ϵ-phase of the alloy with the structure Sb_2Sn_3 at concentrations below 0.4 atomic fraction of antimony. Using the quasi-chemical formulation for compound forming alloys, the assumption of a complex of the form Sb_2Sn_3 could not reproduce effectively and simultaneously the measured activity and free energy of mixing for this liquid alloy at 770 K. Other choices of complexes of the form $Sb_\mu Sn_\nu$ (where μ and ν can take values of 1, 2, and 3) also failed to reproduce simultaneously the measured thermodynamic data except for the choice of the complex of the form $SbSn_2$ (where $\mu = 1$ and $\nu = 2$) which reproduced effectively the measured thermodynamic properties of this alloy at a temperature of 770 K. This is shown in figures 1 and 2. The points represent experimental values from the work of [15]. The energy parameters used for this calculation for Sb–Sn liquid alloys are

$$\frac{w}{kT} = -1.07, \quad \frac{\Delta\epsilon_{ab}}{kT} = -0.06, \quad \frac{\Delta\epsilon_{aa}}{kT} = 0.00, \quad \frac{\Delta\epsilon_{bb}}{kT} = 0.10.$$

On the other hand, the quasi-chemical formulation for compound forming alloys was unable to reproduce the measured thermodynamic properties of the In–Sn liquid alloy for any choice of complexes made. Hence the formulation for the simple regular liquid binary alloy was used for this alloy. This formulation requires only one parameter to reproduce the measured activity and free energy of mixing of the alloy simultaneously. Using the energy parameter $w/kT = -0.10$, the formulation reproduced effectively the measured thermodynamic values as shown in figures 1 and 2. Here the points are experimental values derived from ref. [16]. The figures show that while the activity of Sb–Sn showed some deviation from ideality, the values for In–Sn is very close to ideal. The free energy of mixing for Sb–Sn is asymmetric about equiatomic concentration while that of In–Sn is very symmetric. This deviation from ideal behaviour of the thermodynamic properties of Sb–Sn is due to the intercomponent interaction of the alloy components. Our study therefore suggests some intercomponent interactions existing as a complex of the form $SbSn_2$.

To determine the level of complex activities in the bulk of these alloys throughout the concentration range, the concentration fluctuation at the long wavelength limit
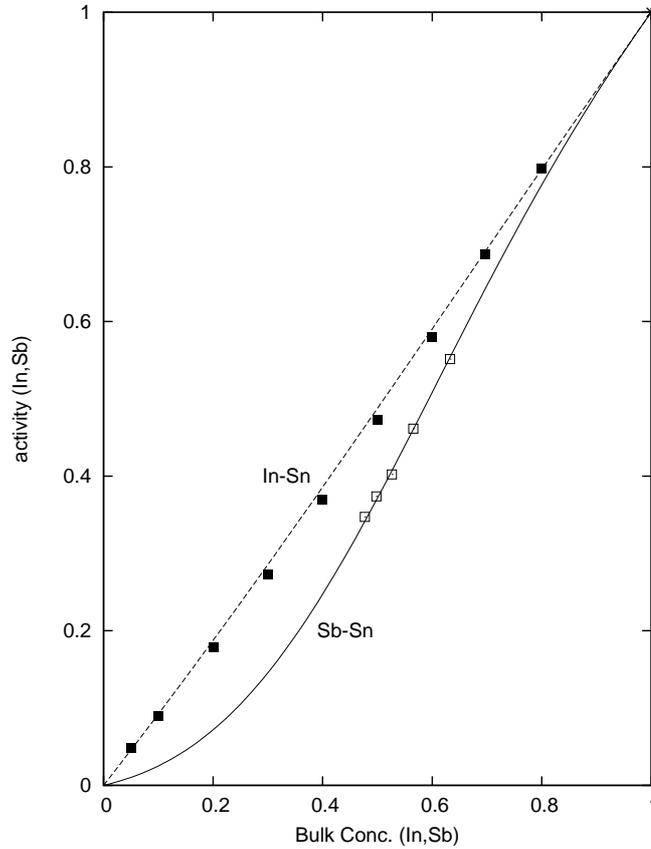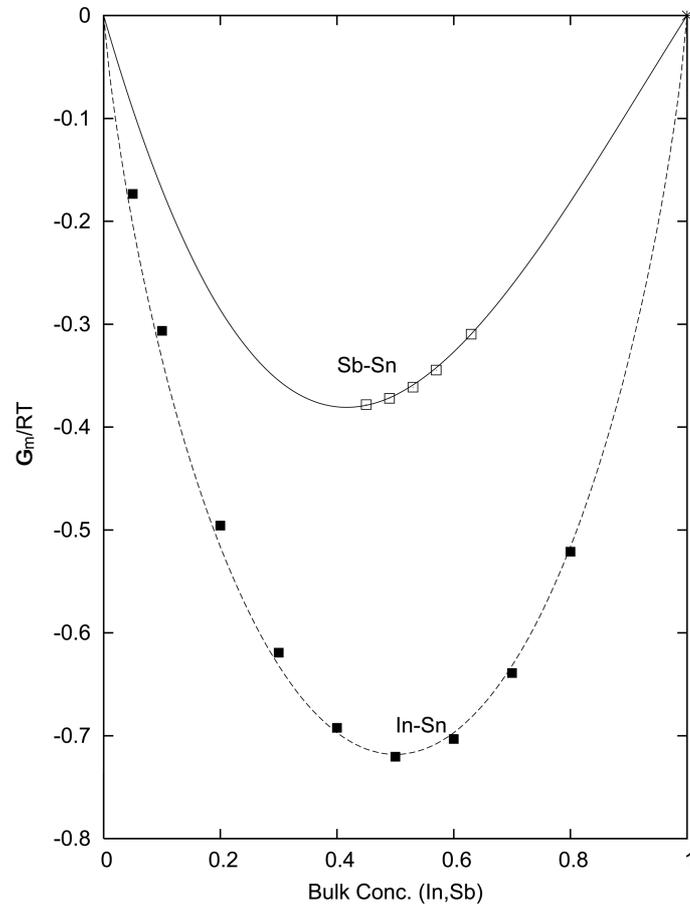
Figure 1. Activity vs. bulk concentration of In and Sb for In–Sn and Sb–Sn liquid alloys respectively. Lines represent calculated activity values. Points are experimental values at 770 K due to refs [12] and [13] respectively.

$S_{cc}(0)$ and the Warren–Cowley short-range order parameter (α_1) for these alloys were calculated. The $S_{cc}(0)$ indicates the kind of local order and the level of complex activities present in the alloy. In general for a liquid binary alloy, when $S_{cc}(0) > S_{cc}^{id}(0)$, the liquid alloy exhibits homocoordination, where $S_{cc}^{id}(0)$ is the ideal value of $S_{cc}(0)$ given by $S_{cc}^{id}(0) = x(1-x)$ and x is the concentration of the A atom in an A–B liquid alloy. When $S_{cc}(0) < S_{cc}^{id}(0)$, the liquid alloy manifests heterocoordination and when $S_{cc}(0) = S_{cc}^{id}(0)$, the liquid alloy is a regular alloy exhibiting a random mixture of components.

The plots of the $S_{cc}(0)$ and the Warren–Cowley short-range order parameter (α_1) for the whole concentration range are given in figure 3. The points represent the experimental values of $S_{cc}(0)$ determined by fitting the experimental activity values to a higher order polynomial and obtaining $S_{cc}(0)$ by evaluating the expression

$$S_{cc}(0) = \frac{(1-x)a_m}{(\partial a_m/\partial x)_{T,P}}. \tag{24}$$

Figure 2. Free energy of mixing G_m/RT vs. bulk concentration of In and Sb for In–Sn and Sb–Sn liquid alloys respectively. Lines represent calculated values. Points represent experimental values at 770 K due to refs [12] and [13] respectively.

This method of determining the experimental values of $S_{cc}(0)$ is always used as an alternative approach where the Darkens excess stability values are not available. In the figure, the calculated $S_{cc}(0)$ for the two alloys show good qualitative agreement with the values deduced from experiment. While the $S_{cc}(0)$ values for In–Sn approaches close to ideal values, the values for Sb–Sn manifests asymmetry and suggest a higher level of interaction below 0.4 atomic fraction of antimony. This suggested increase in the level of interaction at concentrations below 0.4 atomic fraction of Sb probably results from compound formation in the alloy. This compound formation may be associated with the presence of the strong ϵ-phase (Sb_2Sn_3) present in the alloy below the liquid phase within the mentioned concentration range. It can be inferred that at an elevated temperature of about 770 K, the ϵ-phase (Sb_2Sn_3) may have dissociated to a simpler complex of the form
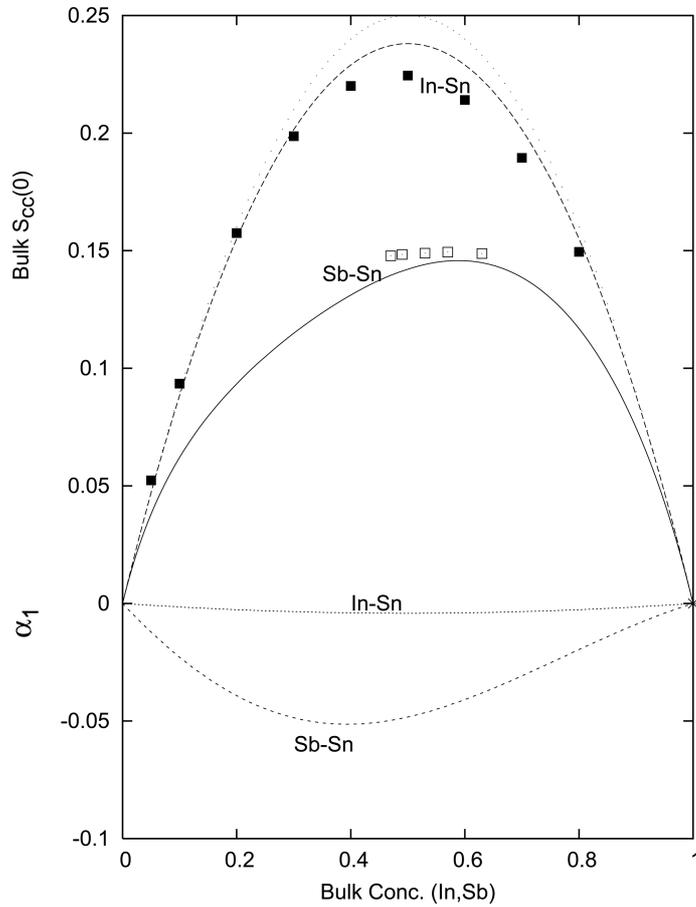
Figure 3. Bulk $S_{cc}(0)$ and α_1 vs. bulk concentration of In and Sb for In–Sn and Sb–Sn liquid alloys respectively. Lines represent calculated values of $S_{cc}(0)$. Points represent experimental values of $S_{cc}(0)$ at 770 K derived from the data of refs [12] and [13] respectively. (- - -) Calculated values of α_1, ($\cdots$) ideal values of $S_{cc}(0)$.

SbSn$_2$. This study suggests that about the temperature of 770 K, the complex SbSn$_2$ may be predominant below 0.4 atomic fraction of antimony. However, the level of interaction of this complex is very low. This can be easily seen from the plot of the Warren–Cowley short-range order (α_1) given in figure 3. The figure showed that Sb–Sn exhibited a minimum value of α_1 as $\alpha_1^{\min} \approx -0.046$ and In–Sn showed $\alpha_1^{\min} \approx -0.004$. These values are very small compared to the value of α_1 for complete order which is $\alpha_1^{\min} = -1.0$.

The surface properties of Sb–Sn and In–Sn liquid alloys were computed numerically from the expressions in eqs (20) and (21). The activity coefficients for Sb, In and Sn were computed from expressions in eq. (13) using the energy parameters previously determined for each set of alloys. The surface coordination fractions p
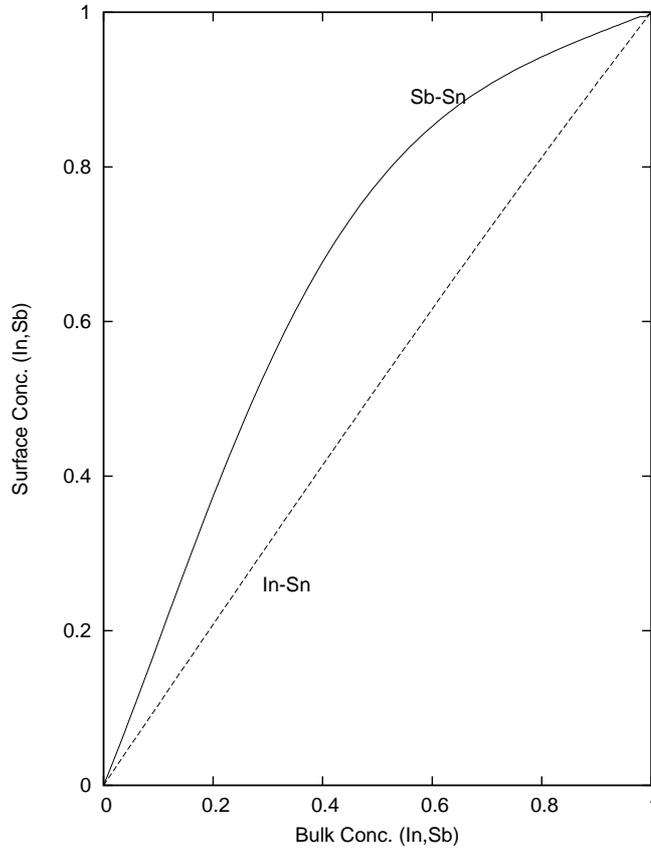
Figure 4. Surface concentration of In and Sb vs. bulk concentration of In and Sb for In–Sn and Sb–Sn liquid alloys respectively.

and q are taken as those for close packed structures with $p = 0.5$ and $q = 0.25$. The surface tension (ζ_i) and atomic volume (Ω_i) at the melting temperatures of the components of the alloy system were taken from [18] (where i denotes Sb, In or Sn). However, to obtain the surface tension and atomic volumes at the working temperature of 770 K, the relationship on the temperature dependence of surface tension and atomic volumes of liquid metals were used as given in [19]:

$$\zeta_i = \zeta_{\mathrm{im}} + (T - T_{\mathrm{m}})\frac{\partial \zeta_i}{\partial T} \tag{25}$$

and

$$\Omega_i = \Omega_{\mathrm{im}}\left[1 + \theta(T - T_{\mathrm{m}})\right], \tag{26}$$

where θ is the thermal coefficient of expansion, Ω_{im}, ζ_{im} are the atomic volumes and surface tension of the alloy components at melting temperature T_{m}. T is the working temperature. Both T_{m} and T are in Kelvin. The values of $\partial \zeta_i / \partial T$ and θ
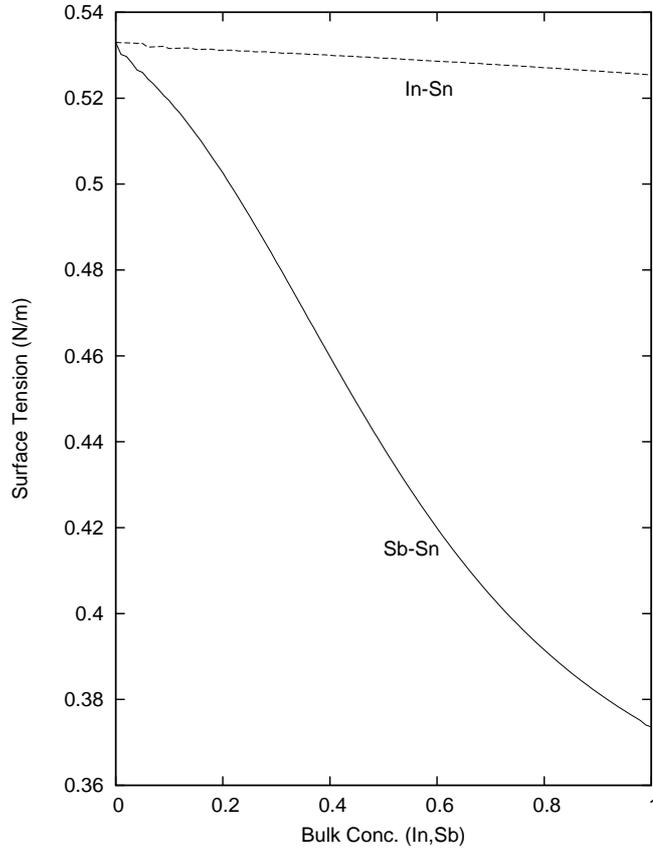
Figure 5. Surface tension vs. bulk concentration of In and Sb for In–Sn and Sb–Sn liquid alloys respectively.

for the pure alloy components were obtained from ref. [18]. The atomic surface area ξ_i for each atomic species of the different alloy systems was calculated following the relation [20]
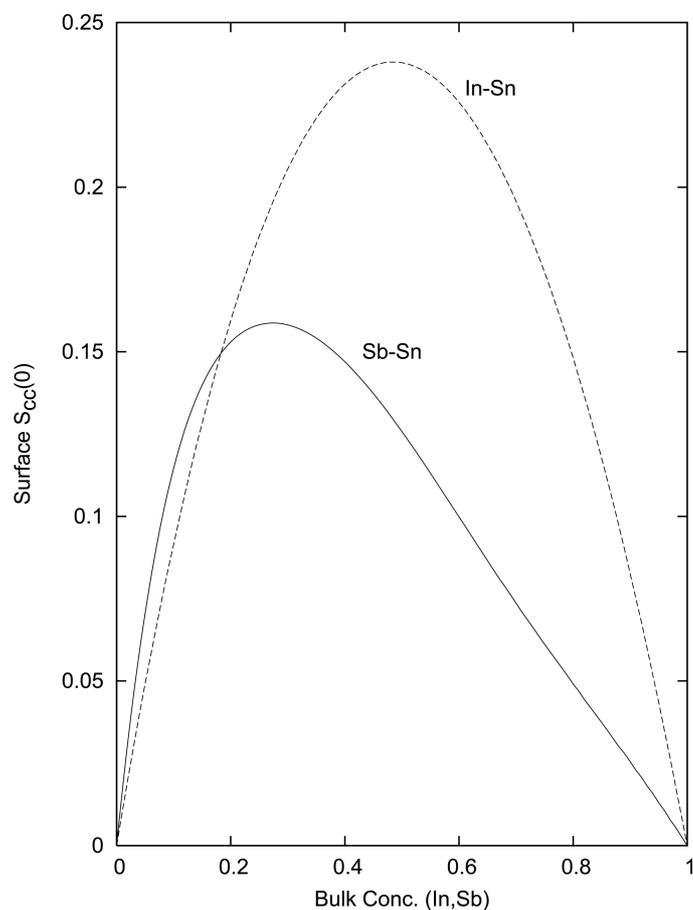
$$\xi_i = 1.102 \left(\frac{\Omega_i}{N}\right)^{2/3} \tag{27}$$

and the mean surface area ξ is given as

$$\xi = \sum_i x_i \xi_i, \tag{28}$$

where N is the Avogadro number and x_i are the concentrations of the alloy components.

The variation of surface concentration of Sb and In against their bulk concentration is given in figure 4. For the Sb–Sn alloys, more Sb atoms are present at the

Figure 6. Surface $S_{cc}(0)$ vs. bulk concentration of In and Sb for In–Sn and Sb–Sn liquid alloys respectively.

surface than Sn atoms especially for concentration greater than 0.5 atomic fraction of Sb. In–Sn alloys show proportionate ideal mixing of alloy components at the surface for all concentrations. The surface tension values for In–Sn show similar behaviour of an alloy of ideal mixture while the values for Sb–Sn showed a slight positive deviation from ideal behaviour below equiatomic composition and a slight negative deviation from ideal behaviour above equiatomic composition of Sb (figure 5). However, in general the surface tension values for Sb–Sn is close to ideal behaviour. The presence of the complex SbSn$_2$ has very little influence on the surface tension of this alloy. This may be because of the weak nature of the complex.

To predict local order on the surface of the alloy, the surface $S_{cc}(0)$ was computed and plotted against the bulk concentrations for the alloys in figure 6. This figure shows that In–Sn also showed tendencies of ideal mixing at the surface with a symmetric shape of its surface $S_{cc}(0)$. The surface $S_{cc}(0)$ for Sb–Sn is skewed to the lower concentrations of antimony. Its deviation from the ideal $S_{cc}(0)$ with usual

maximum value of 0.25, signifies some level of heterocoordination at the surface which does not appear very strong.

4. Conclusion

Sb, In and Sn are close neighbours in the same period on the periodic table. Alloy components made from them manifest features which are not very close. While In–Sn shows the behaviour of a regular alloy with ideal mixture of components in all properties investigated, Sb–Sn showed some level of compound formation manifesting asymmetry in its thermodynamic and surface properties.

Acknowledgement

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