RESEARCH ARTICLE

Complex Formation behavior of Copper-Tin Alloys at its Molten State

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DOI: 10.5185/amlett.2021.011595

Thermodynamic and structural properties of compound forming binary liquid copper tin alloy at 1400K have been well analyzed as a function of concentration by considering Cu_3Sn complex by using Quasi lattice model. The mixing behavior of the alloy is studied in detailed by giving more emphasis on the interaction energy parameters between neighboring atoms of the alloy. The study provides the information of moderately interacting as well as ordering nature on the entire range of concentration of the liquid alloy. Similarly transport and surface properties (viscosity surface tension) of the liquid have also been studied under statistical models; Budai-Banko-Kaptay model and Butler's approach. The computed theoretical thermodynamic data of 1400K are in good agreement with the corresponding experimental data. The viscosities and surface tension of the alloys computed predicts noticeable negative derivation from ideal case and these increase with increase in copper atoms in the alloy.

Introduction

The study of mixing properties of metallic solution are prime importance in metallurgical science to design and develop new and reliable materials with desired properties. The external conditions like pressure, temperature as well as internal conditions like arrangement of atoms inside the materials, composition of atoms are key factors that play vital role for strength, stability, electrical resistivity etc. of the materials [**1**]. Therefore, the total knowledge of energetic of the liquid mixtures is essential for the development of materials in metallurgical science. It is not only difficult but nearly impossible to obtain such knowledge from the experimental measurements at all temperatures and at all other conditions as they are expensive and often encounter many difficulties while handling at high temperatures. To overcome this, different theoretician have developed different model to understand the thermodynamic, structural, transport and surface properties of liquid alloys by proposing different modeling equations [**2-5**].

The aim of this article is to carry out a theoretical study of concentration dependence of different properties of mixing of copper –tin alloy by considering the existence of Cu_3Sncomplex by using quasi-lattice approach [**3**] at temperature 1400K. In copper alloys, the copper plays as major part which is related to the human beings from ancient periods. Copper and copper alloys have been widely used in auto mobile industry, communication and electronic industries and so on due to their excellent mechanical properties, good bending proof performance, very high corrosion resistance, high thermal and electrical performance [**6,7**]. Of many alloys of copper, the copper tin alloy has been drawing attention of many researchers for some years. The copper-tin is the key alloy for lead –free soldering as tin is the main component of most of solder materials and copper is the most widely used contract materials. Likewise, copper-tin alloys can be considered as important materials for replacing the graphite anodes of the lithium ion batteries. For example, the compounds like Cu_6Sn_5 are considered as one of the main candidates to increase the storage capacity of such cells and to enhance their cycling stability. Due to its high importance for other many applications, e.g. bronze alloys, it is considered that the copper-tin binary allows has been first investigated more than hundred years ago [**8**].

The model used in the article say that, when atoms of the different element A and B are mixed in liquid state, there is a probabilities of grouping of atoms of like AA, BB and AB. Based on the grouping of the atoms of constituent elements the alloys can be classified in to two main categories, the compound forming alloys (ordering) where unlike atoms tend to be nearest neighbor over like atom and segregating where like atoms tend to be nearest neighbor over like atoms [**9**]. The properties under the study carry the Gibb's free energy of mixing, enthalpy of mixing, entropy of mixing, chemical activity, concentration fluctuation in long wavelength limit, Warren–Cowley short range order parameter and diffusivity of the alloy. Similarly, the temperature and composition dependency of surface tension and viscosity of binary liquid alloys are also studied as these are most desirable in metallurgical science to specify the surface and transport properties of liquid mixture respectively [**10**]. And hence scientists are trying to study these

properties by suggesting different models [**11-16**]. Here we try to study the surface tension and viscosity of the alloy by using Butlers and BBK (Budai –Benko-Kaptay) approaches respectively.

Thermodynamic properties such as free energy of mixture, heat of mixture entropy of mixing, chemical activity provide knowledge on the interaction, stability of phases and bonding strength among the constituent atoms [**17**] whereas information on the structural local ordering atoms in binary alloys in the liquid state is provided by the qualitative analysis of microscopic function; the concentration fluctuation in long wave length limit (Scc(0)) and short range order parameter(α_1). The Scc(0) represents the nature of ordering of the atoms whereasα_1 quantifies the degree of ordering [**18-20**].

For the study of alloys, we don't have direct way to distinguish grouping of constituent atoms. Thus, identification of nearest neighbor pair of atoms is very difficult. To overcome this problem either thermodynamic or microscopic conditions are studied to get information associated with nearest neighbor pairing or interactions [**21**].

The organization of this paper is as follows. In section 2, the expressions required for calculation are presented. In section 3, result and general discussion of alloy Cu-Sn are presented. Finally, the conclusions are given in Section 4.

Theoretical Basis

Thermodynamic functions

Let a binary has two elements A and B with N_A and N_B atoms respectively. Then the model considers the existence of chemical complexes A_xB_y where x and y are the small integers in such a way that

$$xA + yB = A_x B_y$$

With this consideration, grand partition function [**22**] in terms of configurational energy 'E' is expressed as

$$\Xi = \sum_E Q_A^{N_A}(T) Q_B^{N_B}(T) \exp\left[\frac{(\mu_A N_A + \mu_B N_B - E)}{K_B T}\right] \quad (1)$$

When Q_j (T) and μ_j are atomic partition function and chemical potential of the j^{th}(j=A, B) species, K_B is Boltzman constant and T is absolute temperature. By using above relation we find following expressions for the determination of different properties. With this consideration the excess free energy of mixing becomes.

$$G_M^{EXS} = NK_BT \int_0^C \Upsilon \, dC \quad (2)$$

Where Y is ratio of activity coefficient of atom A to B; C is the concentration of atom A.

The solution of equation (2) leads to

$$G_M^{EXS} = N[\Theta\omega + \Theta_{AB}\Delta\omega_{AB} + \Theta_{AA}\Delta\omega_{AA} + \Theta_{BB}\Delta\omega_{BB}] \quad (3)$$

Where ω's are the ordering energies; and Θ = C (1-C) and $\Theta_{j,k}$'s (j,k=A,B) are the simple polynomials in C depending on the values of x and y.

For A = Cu, B = Sn, x = 3, y = 1, the values of $\Theta_{j,k}$'s are found to be [3]

$$\Theta_{AB}(C) = \frac{1}{5}C + \frac{2}{3}C^3 - C^4 - \frac{1}{5}C^5 + \frac{1}{3}C^6$$

$$\Theta_{AA}(C) = -\frac{3}{20}C + \frac{2}{3}C^3 - \frac{3}{4}C^4 + \frac{2}{5}C^5 - \frac{1}{6}C^6$$

$$\Theta_{BB}(C) = 0$$

The Free energy of mixing for complex forming

$$G_M = G_M^{EXS} + G_M^{ideal}$$

$$G_M = G_M^{EXS} + N K_B T[C \ln C + (1-C)\ln(1-C)]$$

$$= RT\left[\Theta \frac{\omega}{K_BT} + \Theta_{AB}\frac{\Delta\omega_{AB}}{K_BT} + \Theta_{AA}\frac{\Delta\omega_{AA}}{K_BT} + \Theta_{BB}\frac{\Delta\omega_{BB}}{K_BT} + C\ln C + 1 - C\ln(1-C)\right] \quad (4)$$

The heat of mixing is found out by using standard thermodynamic relation;

$$\frac{G_M}{RT} = \frac{G_M}{RT} - \left[\frac{1}{R}\frac{dG_M}{dT}\right]_{C,N,P}$$

$$= \Theta\left[\frac{\omega}{K_BT} - \frac{1}{K_B}\frac{d\omega}{dT}\right] + \Theta_{AB}\left[\frac{\Delta\omega_{AB}}{K_BT} - \frac{1}{K_B}\frac{d\Delta\omega_{AB}}{dT}\right] + \Theta_{AA}\left[\frac{\Delta\omega_{AA}}{K_BT} - \frac{1}{K_B}\frac{d\Delta\omega_{AA}}{dT}\right] + \Theta_{BB}\left[\frac{\Delta\omega_{BB}}{K_BT} - \frac{1}{K_B}\frac{d\Delta\omega_{BB}}{dT}\right] \quad (5)$$

The standard thermodynamic relation for entropy of mixing is

$$\frac{S_M}{R} = -\left[\frac{G_M}{RT} - \frac{H_M}{RT}\right] \quad (6)$$

The activity of the constituent elements in the alloys is determined from following standard thermodynamic relation.

$$RT\ln a_j(j = A, B) = G_M + (1-C)\left[\frac{\partial G_M}{\partial C_j}\right]_{T,P,N} \quad (7)$$

By solving equation (4) and (7), the theoretical values of activities of each component are given as follows,

$$\ln a_A = \frac{G_M}{RT} + \frac{1-C}{K_BT}\left[(1-2C)\omega + \Theta'_{AB}\Delta\omega_{AB} + \Theta'_{AA}\Delta\omega_{AA} + \Theta'_{BB}\Delta\omega_{BB} + \ln\frac{C}{1-C}\right] \quad (8)$$

$$\ln a_B = \frac{G_M}{RT} - \frac{C}{K_BT}\left[(1-2C)\omega + \Theta'_{AB}\Delta\omega_{AB} + \Theta'_{AA}\Delta\omega_{AA} + \Theta'_{BB}\Delta\omega_{BB} + \ln\frac{C}{1-C}\right] \quad (9)$$

Where Θ'_{AB} , Θ'_{AA} and Θ'_{BB} are concentration derivatives ofΘ_{AB}, $\Theta_{AA}$and Θ_{BB} respectively

Microscopic functions

The concentration fluctuation in long wavelength limit for alloy is derived from standard relation as [**18**].

$$S_{CC}(0) = RT\left[\frac{\partial^2 G_M}{\partial C^2}\right]^{-1}_{T,P,N}$$

$$C_B a_A\left[\frac{\partial a_A}{\partial C_A}\right]^{-1}_{T,P,N} = C_A a_B\left[\frac{\partial a_B}{\partial C_B}\right]^{-1}_{T,P,N} \quad (10)$$

Where C_A (=C) and C_B (=1-C) are concentrations and a_A and a_B are observed activities of elements A and B respectively.

Solving equations (4) and (7), the theoretical value of Scc(0) is found as follows

$$s_{CC}(0) = \frac{C(1-C)}{1+(1-C)\left[-2\frac{\omega}{K_BT}+\theta''_{AB}\frac{\Delta\omega_{AB}}{K_BT}+\theta''_{AA}\frac{\Delta\omega_{AA}}{K_BT}+\theta''_{BB}\frac{\Delta\omega_{BB}}{K_BT}\right]} \quad (11)$$

Where $\theta''_{j,k}$is second derivative of $\theta_{j,k}$with respect to concentration.

The Warren-Cowley short range order parameter [**19,20**] is related with concentration fluctuation in long wavelength limit as,

$$\alpha_1 = \frac{S-1}{S(Z-1)+1} \quad (12)$$

Where Z is coordination number and

$$S = \frac{S_{CC}(0)}{S^{id}_{CC}(0)} \quad (13)$$

Diffusion coefficient ratio and viscosity

The mixing nature of molten alloy can also be studied at the microscopic level in terms of diffusion coefficient ratio ($\frac{D_M}{D_{id}}$) and viscosity which give idea about atomic transport properties.

The diffusion coefficient ratio is related to concentration fluctuation in long wave length limit as

$$\frac{D_M}{D_{id}} = \frac{S^{id}_{CC}(0)}{S_{CC}(0)} \quad (14)$$

When D_{id} is the intrinsic or self-diffusion coefficient for an ideal mixture and D_M is chemical or mutual diffusion coefficient.

For binary liquid alloy the mutual diffusion coefficient (D_M) is related with activity, self-diffusion coefficient of ideal mixture and concentration as [**23**]

$$D_M = D_{id}C_j\frac{d\ln a_j}{dC_j} \quad (15)$$

Viscosity of the alloy is studied by using BBK (Budai-Benko-Kaptay) model which is given as

$$\eta = P\{T(C_AM_A + C_BM_B)\}^{\frac{1}{2}}(C_AV_A + C_BV_B + V^E)^{\frac{-2}{3}}\exp\left\{\left(C_AT_{m,A} + C_BT_{m,B} - \frac{H_M}{qR}\right)\frac{Q}{T}\right\} \quad (16)$$

Where, P and Q are constants whose values are (1.80 ± 0.39) × 10^{-8} $(JK^{-1}mol^{-1/3})^{1/2}$ and 2.34 ±0.20 respectively, q is semi empirical parameter having value equal to 25.4. Similarly M_K, V_k, $T_{m,k}$, V^E and R respectively molar mass, molar volume, effective melting temperature of constituent elements of the alloy (K=A,B), excess volume of the alloy and universal gas constant.

Surface tension

According to Butler's approach when a solution of the bulk and hypothetical surface are in equilibrium, the surface tension of the solution is given as

$$\tau = \frac{\mu_j^S - \mu_j^b}{A_j} \quad (17)$$

Where, μ_j^b and μ_j^S are chemical potentials in bulk and hypothetical surface respectively, A_j is molar surface area of j^{th} component of the solution.

Butler further considered that the variation of chemical potential with the composition of surface layer in an ideal solution can be written by the same equation in the surface and bulk.

Thus

$$\mu_j^S = \mu_j^{S0} + RT\ln C_j^S \quad (18)$$

And

$$\mu_j^b = \mu_j^{b0} + RT\ln C_j^b \quad (19)$$

In the case of real solution, molar fractions (C_j^S andC_j^b) can be replaced by activity (a_j^s and a_j^b) to describe chemical potential [**24**].

$$\mu_j^S = \mu_j^{S0} + RT\ln a_j^S \quad (20)$$

$$\mu_j^b = \mu_j^{b0} + RT\ln a_j^b \quad (21)$$

After solving above equations (18), (19), (20), (21) we get,

$$\tau = \tau_j^o + \frac{RT}{A_j}\ln\frac{C_j^S}{C_j^b} + \frac{G_j^{S,EXS} - G_j^{b,EXS}}{A_j} \quad (22)$$

Where $G_j^{S,EXS}$ and $G_j^{b,EXS}$ are partial excess free energy of mixing in the surface and bulk of constituent elemennts of the alloy respectively. The molar surface area of component j is given as [**25**].

$$A_j = g\,(V_j^0)(N)^{\frac{1}{3}} \quad (23)$$

Where g, V_j^0 and N are geometrical constant, molar volume of each pure element at its melting point and Avogardo's number respectively. The value of geometrical constant is expressed as,

$$g = (3\frac{f_V}{4})^{\frac{2}{3}}\pi^{\frac{1}{3}}f_S \quad (24)$$

Where f_v and f_s are volume packing fraction and surface packing fraction respectively. Their values are based on the crystal structure type of every pure component of alloys.

Result and discussion

Though the properties of binary alloys vary with temperature, pressure, and composition, the study of the alloy is carried out at fixed atmospheric pressure and at given temperature as a function of concentration or composition. The different results obtained from study are given in the section below.

Thermodynamic properties

For the study of thermodynamic property, we consider equations (4), (5), (6), and (7) as mentioned above. For the free energy of mixing, the energy parameters used in our model are determined by successive approximation method by the help of experimental values in the concentration range 0.1 to 0.9 [**26**]. The approximate values of the parameters are as follows:

$$\frac{\omega}{K_BT} = 2.97\,,\ \frac{\Delta\omega_{AB}}{K_BT} = 0.77\,,\ \frac{\Delta\omega_{AB}}{K_BT} = -8.82 \quad (25)$$

During the calculation of parameters, no any statistical method like mean square deviation is applied in order to decide the best fit so that the parameters used here are considered as reasonable for the study. Similarly, same

theoretical parameters have been considered throughout calculation to make consistency for the study of other mixing properties. The plot of free energy of mixing versus concentration of copper is shown in **Fig. 1**. The computed and experimental value of G_M/R_T are in reasonable agreement. The theoretical value of free energy of mixing is minimum i.e.-1.18RT at 0.6 concentration of Cu. The theoretical calculation of free energy of mixing shows that at liquid state the alloy Cu-Sn is moderately interaction and hence the tendency of compound formation is not so strong, being asymmetry at equi-atomic concentration 0.5, then alloy can be classified as irregular alloy.

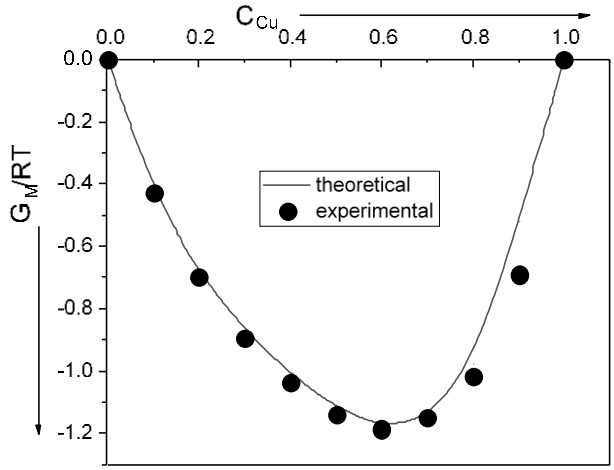

Fig. 1. Free energy of mixing (G_M/RT) versus concentration of copper (C_{cu}) for molten Cu-Sn at 1400 K.

The deviation from ideal behavior of alloy can be explained by chemical activities, a measure of tendency to leave the mixture, as its magnitude depends in the interaction of constituent binary components of the alloy. The Equations (8) and (9) are used for theoretical calculation of chemical activity of constituent element of alloy Cu-Sn. **Fig. 2** shows the observed and theoretical value of chemical activity of the alloy. There is reasonable good agreement between experimental and theoretical value of activities of Cu and Sn in Cu-Sn alloy at 1400K at all concentrations of Cu with very small discrepancies.

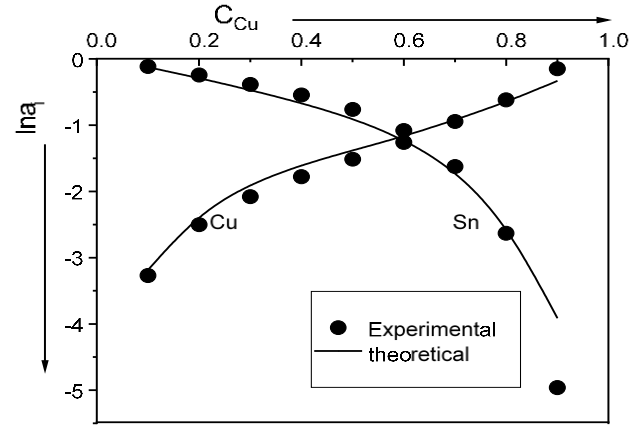

Fig. 2. Chemical activity ($ln\ a_i$) versus concentration of Cu (C_{cu}) of Cu-Sn molten alloy at 1400K.

For the theoretical determination of heat of mixing, temperature derivatives of interaction parameters are required which are obtained from large no of choice of these parameters (i.e. by successive approximation method). The best fit values of parameters are

$$\frac{1}{K_B}\frac{d\omega}{dT} = -1.16,\ \frac{1}{K_B}\frac{d\Delta\omega_{AB}}{dT} = 1.09,\frac{1}{K_B}\frac{d\Delta\omega_{AA}}{dT} = -1.36 \quad (26)$$

The plot of heat of mixing versus concentration of copper is shown in **Fig. 3**. It is found from the analysis that the heat of mixing is more negative towards copper rich region the observed nature of heat of mixing versus concentration of copper curve is well explained by the theory. The computed and experimental value of H_M /RT are in reasonable agreement with some discrepancies.

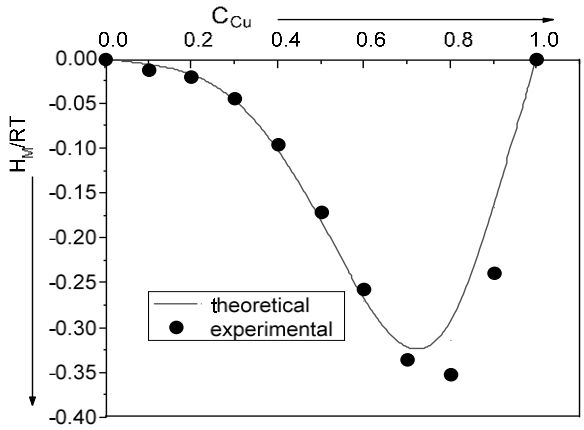

Fig. 3. Heat of mixing (H_M/RT) versus concentration of copper (C_{cu}) for molten Cu-Sn at 1400K.

Using equation (4) and (5), the entropy of mixing (S_M) is computed. For theoretical calculation same energy parameters already used in equation (24) and (25) are used.

The plot of entropy of mixing (S_M/R) versus concentration of copper is shown in **Fig. 4** for both theoretical and observed values. From figure, it is observed that theoretical values are in good agreement with observed values.

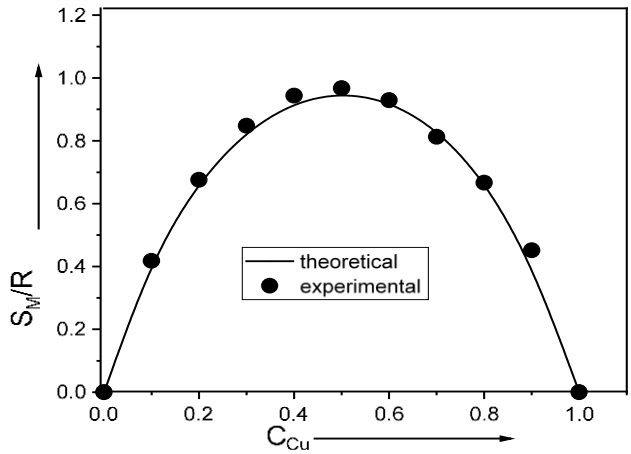

Fig. 4. Entropy of mixing (S_M/R) versus concentration of copper (C_{cu}) for molten Cu-Sn at 1400 K.

Microscopic properties

One of the important function for the study of nature of atomic order of the binary liquid is considered as the Concentration fluctuations in the long-wavelength limit (Scc(0)) because it removes difficulties on diffraction experiment [**18**]. For given concentration if $Scc(0)<S^{id}cc(0)$, the expected nature is complex formation. The experimental and theoretical values of Scc(0) at different concentrations of element copper are obtained from equations (10) and (11) respectively. The plot of experimental and theoretical along with ideal values of Scc(0) versus concentration of Cu is shown in **Fig. 5**.

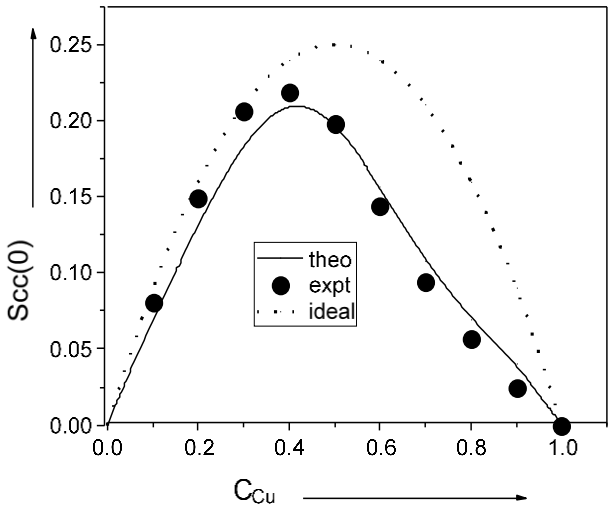

Fig. 5. Concentration fluctuation in long wavelength limit (Scc(0)) versus concentration of copper (C_{cu}) for molten Cu-Sn at 1400 K.

From figure it is clear that the experimental as well as theoretical values of Scc(0) lie below ideal value of Scc(0) throughout whole range of concentration of copper which is the good signature of ordering nature of the alloy.

The Warren-Cowley short-range order parameter (α_1) is other most powerful parameters to provide information of the local arrangement of the atoms in the molten alloys [**19,20**]. Actually, it quantifies the degree of chemical order in the liquid alloys whose value lies between -1 to +1. The negative value of α_1 is indication of ordering nature of the alloy, which is complete for $\alpha_1 = -1$. The value $\alpha_1 = 0$ is the indication of the random distribution of the atoms in the mixture and similarly positive values of α_1 is the indication of segregating nature, which is complete for $\alpha_1 = 1$. The value of α_1 has been computed as a function of concentration of Cu using equation (12). The plot of theoretical values of α_1 versus concentration of Cu is shown in **Fig. 6**. From the figure it is observed that the value of α_1 is negative throughout the whole region of concentration of copper with maximum negative at 0.8 concentration of copper which signifies the strong tendency of ordering nature of the alloy.

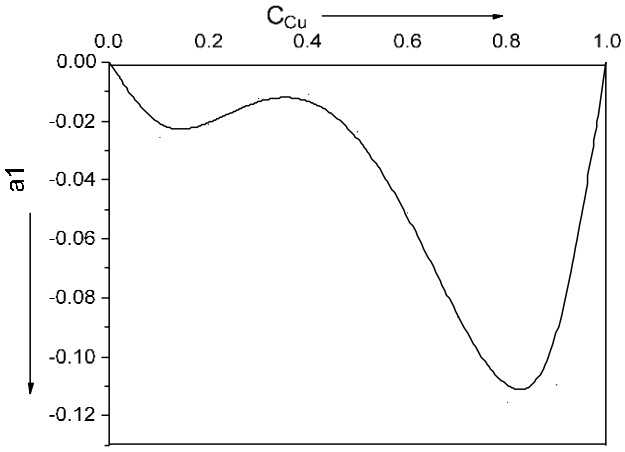

Fig. 6. Warren Cowley short range order parameter (α_1) versus concentration of copper (C_{cu}) for Cu-Sn molten alloy at 1400 K.

Transport Properties: Diffusion coefficient ratio and viscosity

To study the atomic transport properties at microscopic level, the diffusion coefficient ratio and viscosity are studied. The diffusion coefficient ratio, expressed by the ratio of the mutual and self-diffusion coefficients (D_M/D_{id}), is quite good indication of knowledge of the mixing behavior of the alloys, where $D_M / D_{id} > 1$ indicates hetero-coordination nature (i.e. ordering), $D_M / D_{id} < 1$ indicates homo-coordination nature (i.e. Segregating) and $D_M/D_{id} = 1$ indicates ideal mixing of the atoms. The calculated values of Scc(0) are used in equation (15) to determine the ratio of the mutual and intrinsic-diffusion coefficients (D_M/D_{id}).

During the calculation we consider the coordination number Z to be 10. **Fig. 7** shows the plot of D_M/D_{id} against the concentration of copper. In the figure, the value of D_M/D_{id} is found to be more than 1 in the entire range of concentration having maximum value 2.24 at 0.8 concentration of copper which is indication of the compound forming tendency of the alloy.

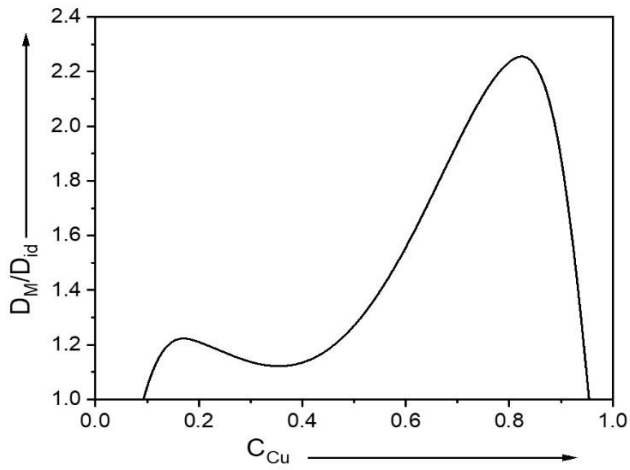

Fig. 7. Diffusion coefficient ratio (D_M/D_{id}) versus concentration of copper (C_{cu}) for Cu-Sn molten alloy at 1400 K.

Viscosity is considered as one of the most valuable thermo-physical properties in metallurgical science that mainly concerns with industrial processes and many natural phenomena. It is related with parameters such as composition of the liquid, cohesion energy and the molar volume [**27,28**]. In our equation (17), the value of V^E is taken as zero. This is due to the fact that there is lack of experimental data and contribution of this term is too small in the range of $10^{-7}m^3$/mole for determination of viscosity [**10,29**]. The compound values of viscosity with concentration as given by BBK model is shown in **Fig. 8**.

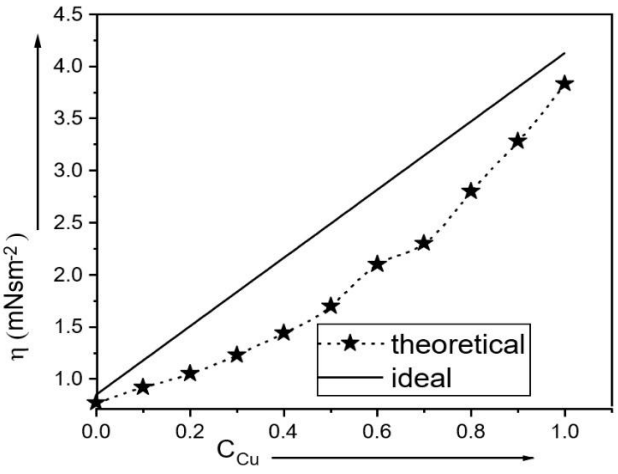

Fig. 8. Viscosity (η) versus concentration of Cu (C_{cu}) of molten Cu-Sn at 1400 K.

Surface properties: Surface tension

In metallurgical science and industry, for the processing as well as for the production of new materials the surface tension of liquid alloy or liquid metal is considered as key factors because it is concerned to the problems related to the surface as well as interface in liquid metal process [**30,31**]. The interfacial motion of liquid caused by surface tension plays a vital role in many industrial phenomena and hence the surface and interfacial features of liquid metals are considered to have great importance in metallurgical process for controlling the processes of welding, casting and solidification [**32**].

To calculate the surface tension of the alloy Cu-Sn by using equation (23), the densities and surface tension of individual metals required at 1400 K are calculated by using relations given in reference [**33**].

The bulk partial excess free energy of mixing of individual copper and tin in liquid state at 1400K is taken from reference [**26**]. The geometrical structure factor and ratio of surface excess energy to the bulk excess ($\frac{G_j^{s,EXS}}{G_j^{b,EXS}}$) are respectively considered as 1.061 and 0.8181 [**25**]. The values of surface tension thus computed are plotted against bulk concentration as shown in **Fig. 9**. From the figure 9, it is observed that the surface tension increases with increase in copper atoms in the alloy but due to lack of experimental data we cannot compare our theoretical results.

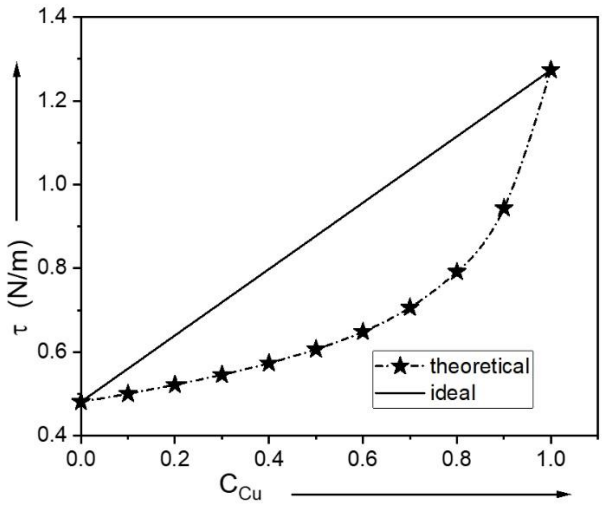

Fig. 9. Surface tension (τ) versus concentration of Cu (C_{cu}) of molten Cu-Sn at 1400 K.

Conclusion

The present study is the theoretical analysis for the understanding of thermodynamic, structural and microscopic behavior of binary liquid copper tin alloy at 1400 K alloy under the assumption of existence of Cu_3Sn complex in the liquid mixture by quasi lattice approximation. The study well explains the asymmetry behavior of the thermodynamic properties as a function of concentration. The theoretical study shows that the alloy has the nature of ordering in the entire range of concentration as well as a moderately interacting system. The viscosity and surface tension of the liquid binary alloy increase with the increase in the concentration of copper component.

Received: 16 May 2020
Revised: 11 June 2020
Accepted: 25 August 2020

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