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The role of size effect on the bulk properties of copper-tin liquid alloys

Awe, O. E.
Department of Physics, University of Ibadan, Ibadan, Nigeria
Corresponding author: draweoe2004@yahoo.com

Abstract

A statistical mechanics model based on complex formation and a Flory's approximate model have been used to theoretically investigate the effect of size difference on the bulk properties of copper-tin liquid alloys, by computing concentration fluctuations in the long wavelength limit, diffusivity, free energy of mixing, integral entropy of mixing and Warren-Cowley short range order parameter of Cu-Sn liquid alloys at 1400K. The results indicate that although, the chemical interactions between copper and tin atoms are quite weak in the entire Cu concentration in the alloys, size effect increase the degree of the interactions in the composition range $C_{cu} \leq 0.75$ and reduces the tendency for heterocoordination in the composition range $0.60 \leq C_{cu} \leq 0.90$. Also, the results reveal further that size effect significantly increase the magnitude of the integral entropy of mixing of Cu-Sn liquid alloys in the composition range $C_{cu} \geq 0.30$ and that the contributions of ideal entropy of mixing, temperature dependent interchange energy and size difference to the integral entropy of mixing are quite significant and complementary. The study further indicate that Flory's approximate model, possibly has significant limitation.

Keywords: Bulk properties; Cu-Sn; liquid alloy; size difference.

Introduction

Cu-Sn alloy, otherwise known as tin bronze, is reported to be the oldest metal material in the world and has contributed significantly towards the evolvement of human civilization, especially during the Bronze Age [1]. Up till date, bronze containing primarily Cu and Sn with the addition of other metals or non-metals/ metalloids are still being widely used to manufacture various mechanical parts due to their excellent wear resistance and sufficient strength and ductility [1, 2]. Hence, Cu-Sn alloys have been studied for the past thousands of years, from ancient time to modern industry [3,4].

In the past few decades, many researchers have shown sustained interest in Cu-Sn liquid alloys with the aim of understanding either the cause of asymmetry in the observed concentration dependence of thermodynamic and microscopic properties of Cu-Sn liquid alloys, or the cause of de-wetting characteristics of Cu-Sn after being used in soldering [5-8]. This aforementioned interest in understanding the cause of asymmetry/anomaly is a function of the fact that without such understanding, we cannot get the real picture of the mixing behaviour, which is crucial for industrial applications [5].

However, our search of literatures show that an investigation of the contribution of size effect to the asymmetry in the concentration dependence of thermodynamic and microscopic properties of Cu-Sn liquid alloys are yet to be undertaken. This observation is quite surprising because Bhatia [9] reported that in line with the ideas in electron theory, an asymmetry in energy of mixing (or mixing property) can be due to difference in the Hume-Rothery empirical factors such as valency, electronegativity and sizes of the two types of atoms in a binary alloy [10]. Hence, on the premise of this report, coupled with the fact that the size difference between Cu and Sn atoms in Cu-Sn is 2.14 which is greater than the 2.0 criterion (i.e. size effect is usually assumed to be negligible if the size difference

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is less or equal to 2.0) [11], we are of the opinion that an investigation of the effect of this significant size difference on the bulk properties of Cu-Sn liquid alloys, worth being done.

In order to study the bulk properties of Cu-Sn liquid alloys, we used two different empirical thermodynamic models, in a way similar to what were done in [11-14]. The choice of models was informed by the appropriateness of the model to the alloy and the focus of this research. Thus, we employed Flory's approximate model (known for incorporating size effect in the computation of thermodynamic properties of liquid binary alloys) and the complex formation model (which does not incorporate size effect factor in the computation of thermodynamic properties of liquid binary alloys).

The arrangement of the paper is as follows. We present the essential formalism (in the form of material and methods) of the bulk properties in the next section. The results we obtained are presented and discussed in Section 3. The paper is concluded in Section 4.

Material and methods

The available experimental data of Cu-Sn alloys obtained from [15] shows that in the entire composition of Sn, the free energy of mixing G_M and the excess free energy of mixing G_M^{xs} are negative; the integral entropy of mixing S_M/R and the excess integral entropy of mixing S_M^{xs}/R are positive while the integral enthalpy of mixing H_M/RT has negative and positive values.The phase diagram shows intermetallic compounds such as $Cu_{31}Sn_8$(δ phase at 850 K), $Cu_{20}Sn_6$ (ξ phase at 913 K), Cu_3Sn (ε phase at 850 K)and Cu_6Sn_5(η phase at 688 K).In this work, we assume that Cu_3Sn persists in the liquid phase in agreement with the reports in Refs. [5–7,16]. Hence, we can write the following equation:

$$\mu Cu + v\,Sn = Cu_{\mu}Sn_{v}, u = 3 \text{ and } v = 1 \qquad \ldots.1$$

Bhatia and Singh in [17] had shown that the thermodynamic properties of compound-forming E-D alloys can be explained in terms of the energetics of the complexes in Eq. (1) if we use a quasi-lattice model which considered each of such alloys as a pseudoternary mixture of E atoms, D atoms and $E_{\mu}D_{v}$ complexes [18]. The formalism resulting from this, which reduces to Conformal and Flory's approaches for coordination number z = 2 and ∞, respectively, is known as Complex Formation Model (CFM). For the purpose of brevity and to avoid unnecessary repetition of what is very common in the literatures, we shall present only the essential equations relevant to our investigation. Additional information about the model which in our opinion need not be repeated here for brevity, can however, be obtained from any of the Refs. [5, 6, 10, 18, 19].

If N is the total number of atoms in the alloy E-D, Nc is the number of E atoms, N(1-c) is the number of D atoms, c is the concentration of E atoms, W_1 is the individual E atoms, W_2 is the individual D atoms, W_3 is the number of complexes of the type $E_{\mu}D_{v}$ in the melt, then, from the conservation of atoms:

$$W_1 = Nc - \mu W_3 \qquad \ldots.2$$

$$W_2 = N(1-c) - vW_3 \qquad \ldots.3$$

$$W = W_1 + W_2 + W_3 = N - (\mu + v - 1)W_3 \qquad \ldots.4$$

The Gibbs free energy of mixing, G_M which reveals information on the nature of the atomic interactions in an alloy E-D is given by [19]:

$$G_M = -W_3 g + \Delta G \qquad \ldots.5$$

Where g is the formation energy of the complex, –W_3g is the lowering of the free energy due to the formation of complexes in the alloy and ΔG is the free energy of mixing of the ternary mixture of fixed W_1, W_2 and W_3, where constituents E, D and $E_{\mu}D_{v}$are assumed to interact relatively weakly with one another since any strong bonding interaction between E and D atoms has been taken care of via the formation of the complexes [5, 18].

When the expression of ΔG is substituted in Eq. 5, the complete expression for G_M in CFM is given by [5]:

$$G_M = -W_3 g + RT[W_1 \ln W1 + W_2 \ln W_2 + W_3 \ln\{W_3(\mu + v)\}] + \sum_{i<j}\sum W_i W_j W_{ij} \qquad \ldots.6$$

Where R is the molar gas constant, T is the temperature and the V_{ij}s are the interaction parameters.

The equilibrium values of W_3 needed in the computation of G_M given in Eq. 6 is usually obtained from the condition [5, 19]:

$$\left(\frac{\partial G_M}{\partial W_3}\right)_{T,P,N,c} = 0 \qquad \ldots.7$$

Where P is the pressure.

A closer study of Eqns. 6 and 7 shows that the values of W_3 can be obtained when the following equation is solved [19]:

$$\frac{W_1^{\mu} W_2^{\nu}}{W_3 W^M} = \chi e^Y \qquad \ldots .8$$

Where

$$\chi = \exp\left(\frac{-g}{RT}\right), \quad M = \mu + \nu - 1 \qquad \ldots .9$$

and

$$Y = \frac{1}{WRT}\left\{V_{12}\left[M\frac{W_1 W_2}{W} - \mu W_2 - \nu W_1\right] + V_{13}\left[M\frac{W_1 W_3}{W} - \mu W_3 + W_1\right] + V_{23}\left[M\frac{W_2 W_3}{W} - \nu W_3 + W_2\right]\right\} \qquad \ldots .10$$

G_M is finally obtained from Eq. 6 when Eq. 8 is solved numerically to obtain the equilibrium values of W_i (i = 1, 2, 3) for given energy parameters g and V_{ij}.

Another bulk thermodynamic quantity of interest is the concentration-concentration fluctuations in the long wavelength limit $S_{cc}(0)$. This quantity has become a powerful and essential parameter relevant for the understanding of the nature of chemical order and tendency for the phase segregation in binary liquid alloys [5]. $S_{cc}(0)$ is also known for being useful in shedding needed lights on many properties of binary liquid alloys (such as glass forming tendency, diffusion and viscosity) important for industrial applications [5]. It is known from Ref. [20] that, if at a given composition in a liquid alloy, $S_{cc}(0) \gg S_{cc}(0, id)$, (where $S_{cc}(0,id)$ is the ideal $S_{cc}(0)$ whose magnitude is c(1-c)), there is a tendency for segregation or phase separation (the tendency for an E-E or D-D pairs of atoms being preferred over E-D pairs as nearest neighbours in an E-D liquid alloy).On the other hand, if at a given composition in a liquid alloy, $S_{cc}(0) \ll S_{cc}(0, id)$, there is tendency for strong association or existence of chemical complexes in the mixture (the tendency for an E-D pairs of atoms being preferred over E-E or D-D pairs as nearest neighbours in an E-D liquid alloy) [20].The thermodynamic relationship between G_M and $S_{cc}(0)$ is given by

$$S_{cc}(0) = \frac{RT}{\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}} \qquad \ldots .11$$

If the expression for G_M in Eq.(6) is put in Eq. 11, then, we shall obtain the following final expression for $S_{cc}(0)$ in CFM [5]:

$$S_{cc}(0) = \frac{1}{\left\{\sum_{i=1}^{i=3}\frac{(W_i')^2}{W_i}\right\} + (2/RT)\Sigma\Sigma i < j\, W_i' W_j' V_{ij}} \qquad \ldots .12$$

Warren-Cowley short range order parameter α_1 is an important quantity for quantifying the degree of homocoordination/segregation or heterocoordination/ chemical ordering in molten alloys [5]. From [20], we know that $\alpha_1 = 0$, is an indication of random distribution of atoms in the melt; $\alpha_1 > 0$ implies homocoordination in the melt while $\alpha_1 < 0$ is an indication that there is heterocoordination in the melt.

According to Singh *et al* in [21], α_1 and $S_{cc}(0)$ are related by:

$$\alpha_1 = \frac{H-1}{H(Z-1)+1}, \quad H = \frac{S_{cc(0)}}{S_{cc}(0,id)} \qquad \ldots .13$$

Where Z is the coordination number and its value is often taken as 10 [22] and in this work we used Z = 10 (it had been reported in [6] that varying Z only meant varying the depth of α_1 and that the overall feature of α_1 is un-affected by changes in Z). When Eq. 12 and $S_{cc}(0,id)$ = c(1-c) are substituted in Eq. 13, a final expression for α_1 in the CFM will be obtained as

$$\alpha_1 = \frac{\left\{\left(\left[\frac{1}{\left\{\sum_{i=1}^{i=3}\frac{(W_i')^2}{W_i}\right\} + (2/RT)\Sigma\Sigma i < j\, W_i' W_j' V_{ij}}\right] \Big/ c(1-c)\right) - 1\right\}}{\left\{\left(\left[\frac{1}{\left\{\sum_{i=1}^{i=3}\frac{(W_i')^2}{W_i}\right\} + (2/RT)\Sigma\Sigma i < j\, W_i' W_j' V_{ij}}\right] \Big/ c(1-c)\right)(z-1)\right\} + 1} \qquad \ldots .14$$

The expression in the CFM for the integral entropy of mixing S_M which is a thermodynamic quantity that contains the entropic effect (or size difference factor) contribution to Gibbs free energy of mixing in a mixture [23] is obtained from the thermodynamic relation [24]:

$$S_M = \left(\frac{\partial G_M}{\partial tT}\right)_{P,\ c,\ W_3,\ N} \quad \ldots.15$$

If Eq. 6 is substituted in Eq.15, we shall obtain a final expression for the S_M in CFM given by [5]:

$$S_M = -W_3 g' + R\{W_1 \ln W_1 + W_2 \ln W_2 + W_3 \ln[W_3(\mu+\nu)]\} - \sum\sum_{i<j} W_i W_j V'_{ij} \quad \ldots.16$$

Where

$$g' = \frac{\partial g}{\partial T} \quad \ldots.17$$

$$V'_{ij} = \frac{\partial V_{ij}}{\partial T} \quad \ldots.18$$

A transport property which is useful in the study of mixing behaviour of alloys is the ratio of diffusion coefficients, otherwise known as diffusivity, D_M/D_S [25]. This property is related to $S_{cc}(0)$ as follows [26]:

$$\frac{D_M}{D_S} = \frac{S_{cc}(0,id)}{S_{cc}(0)} \quad \ldots.19$$

Where D_M is the mutual diffusion coefficient and D_S is the self-diffusion coefficient or intrinsic diffusion coefficient for an ideal mixture. $D_M/D_S > 1$ is an indication of the tendency for compound formation (heterocoordination), $D_M/D_S < 1$ means tendency for segregation, while $D_M/D_S = 1$ is a signature of ideal mixing.

Having presented all the relevant equations for the use of CFM in this work, we shall now present the counterpart equations in the Flory's approximate model which we also used in our investigation of the role of size effect on the bulk properties of Cu-Sn liquid alloys.

Bhatia and March in [27] had reported that when the size or volume ratio r of E atom and D atom in a E-D alloy is greater or equal to 2.0, the resulting G_M if there are c g moles of E atoms and (1-c) g moles of D atoms is given by [27]:

$$G_M = RT[c\ln\psi + (1-c)\ln(1-\psi)] + f'\psi(1-\psi)$$
$$[r_E c + r_D c(1-c)] \quad \ldots.20$$

Where

$$\psi = \frac{r_E c}{r_E c + r_D(1-c)} \quad \ldots.21$$

$$1-\psi = \frac{r_D(1-c)}{r_E c + r_D(1-c)} \quad \ldots.22$$

If we let

$$f = r_E f' \quad \ldots.23$$

$r = \frac{R_D}{r_E}$, the atomic volumes ratio and $r_D > r_E$ 24

Then, a final expression for G_M in the Flory's approximate model is obtained as [27]:

$$G_M = RT\left\{c\ln c + (1-c)\ln(1-c) - c\ln r - \ln(1-\beta c) + \frac{Wc(1-c)}{(1-\beta c)}\right\} \quad \ldots.25$$

Where $\beta = (r-1)/r$ and $W = f/RT$

If we use the basic thermodynamic relation in Eq.11, we shall obtain the following expression for $S_{cc}(0)$ in the Flory's approximate model [11, 27]:

$$S_{cc}(0) = \frac{c(1-c)}{1-c(1-c)t(c)} \quad \ldots.26$$

Where

$$t(c) = \frac{c + \left\{\left(\frac{2}{\beta^3}\right)(1-\beta)W - \left(\frac{1}{\beta}\right)\right\}}{\left\{\left(\frac{1}{\beta}\right) - C\right\}^3} \quad \ldots.27$$

The expression for α_1 in the Flory's approximate model, using the reasoning similar to that used in Eq. 13 is given by [11]:

$$\alpha_1 = \frac{H^* - 1}{H^*(Z-) + 1} \quad \ldots.28$$

Where

$$H^* = \frac{\dfrac{c(1-c)}{1-c(1-c)t(c)}}{S^*_{cc}(0,id)} \quad \ldots.29$$

Where

$$S^*_{cc}(0,id) = \frac{c(1-c)}{1-c(1-c)\dfrac{\beta c-1}{\beta\left(\dfrac{1}{\beta}-c\right)^3}} \quad \ldots.30)$$

The expression for integral entropy of mixing in the Flory's approximate model is obtained from the thermodynamic relationin Eq. 15.

If Eq. 25 is put in Eq.15, we shall obtain the following final expression for S_M in the Flory's approximate model [24]:

$$S_M = -R\alpha_1(c) - R\alpha_2(c) - c(1-c)\alpha_3(c)\frac{\partial W}{\partial T} + RTc(1-c)\alpha_3(c)\left[\frac{\beta}{1-\beta} - c\alpha_3(c)W/RT\right]\frac{\partial\beta}{\partial T} \quad \ldots.31$$

Where

$$\alpha_1(c) = c\ln c + (1-c)\ln(1-c) \quad \ldots.32$$

$$\alpha_2(c) = c\ln(1-\beta) - \ln(1-\beta c) \quad \ldots.33$$

$$\alpha_3(c) = \frac{1}{(1-\beta c)} \quad \ldots.34$$

The expression for diffusivity in Flory's approximate model is similar to that in Eq. 19.The difference lies in the expressions for $S_{cc}(0)$ and $S_{cc}(0,id)$ which are now given by Eqns. 26 and 30, respectively. Thus, the expression of diffusivity in Flory's approximate model is given by:

$$\frac{D_M}{D_S} = \frac{c(1-c)}{1-c(1-c)t(c)} \Bigg/ \left(\frac{c(1-c)}{1-c(1-\varepsilon)\dfrac{\beta c-1}{\beta\left(\dfrac{1}{\beta-c}\right)^3}}\right) \quad \ldots.35$$

Results and discussion

Equation 8 was solved to obtain values of W_3, g and V_{ij}s that fit well the G_M and $S_{cc}(0)$ in the whole composition range. The values of these parameters used for the computations of G_M, $S_{cc}(0)$, α_1 and D_M/D_S for Cu-Sn liquid alloys at 1400 K,in the framework of CFM are shown in Table 1.The results of the computations are shown in Figures 1-4 and labelled as No-Size-Effect (NSE). Also, Eq. 16 was used in the computation of S_M for Cu-Sn liquid alloys at 1400 K. The temperature derivatives of the energy parameters that gave reasonable fit for the available S_M were used in conjunction with W_3, g and V_{ij}s earlier obtained for G_M, $S_{cc}(0)$, α_1 and $D_M/D_{S,}$ as was equally done in [5]. The values of the temperature derivatives used for the computation of S_M in the framework of CFM are shown in Table 1 while the result of the computation is shown in Figure 5 as NSE.

On the other hand, we obtained the value of the two fitting parameters, r and W/RT needed for the computations of G_M, $S_{cc}(0)$, α_1 and D_M/D_S in the framework of Flory's approximate model as follows:

i. r was obtained from the atomic volumes of pure Cu and Sn at their respective melting points from [28].

ii. W/RT was obtained from the simultaneous fit of G_M and S_{cc} (0), using their experimental values.

The values obtained for these parameters are shown in Table 1 while the results of the computations are shown as With-Size-Effect (WSE) in Figsures 1-4. Also, the values of the two fitting parameters ($\frac{\partial\beta}{\partial T}$ and $\frac{\partial W}{R\partial T}$) needed for the computation of S_M in the framework of Flory's approximate model were obtained from the values that gave a reasonable fit for the available experimental data of S_M in conjunction with the W/RT earlier obtained for G_M, S_{cc} (0), α_1 and D_M/D_S. These values are shown in Table 1 while the result of the computation is shown in Fig.5 as WSE.

A look at Figures 1, 2 and 5 shows that the agreement between the computed and experimental G_M, $S_{cc}(0)$ and S_M, using both CFM and Flory's model are quite good. Although, the degree of the aforementioned agreement is not the same in the two models, in our opinion, our choice of the fitting parameters is okay for the two models.

In Figure 1, we observed that the maximum magnitude of G_M (1.0745 in NSE (i.e. CFM plot) at

Table 1. Essentials parameters for the computation of bulk properties of Cu-Sn liquid alloys at 1400 K, using Complex formation and Flory's approximate models.

Complex formation model		**Flory's model**	
$\mu = 3$,	$\nu = 1$	$r = 2.14$	
$\frac{g}{RT} = 1.70$,	$\frac{V_{12}}{RT} = -0.80$	$\frac{W}{RT} = -1.0970$	
$\frac{V_{13}}{RT} = 0.10$,	$\frac{V_{23}}{RT} = -0.70$		
$\frac{\partial g}{RT} = -1.00$,	$\frac{\partial V_{12}}{RT} = -1.10$	$\frac{1 \partial W}{R \partial T} = -0.5710$	$\frac{\partial \beta}{\partial T} = -0.0$
$\frac{\partial V_{13}}{RT} = 0.50$,	$\frac{\partial V_{23}}{RT} = -1.90$		

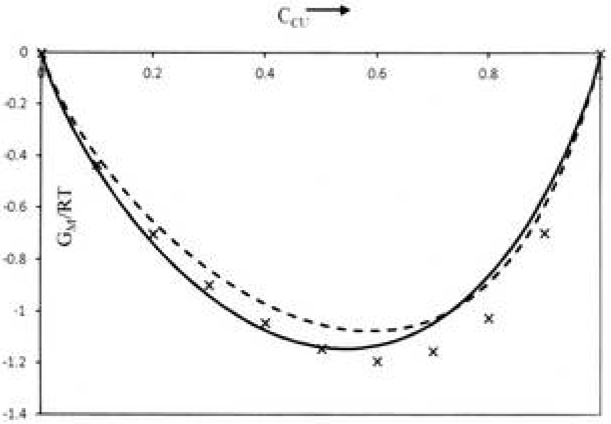

Figure 1. Concentration dependence of GM/RT for Cu-Sn liquid alloys at 1400K. The solid line represents WSE while the dashes represent NSE. The times represent experimental values obtianed from [15].

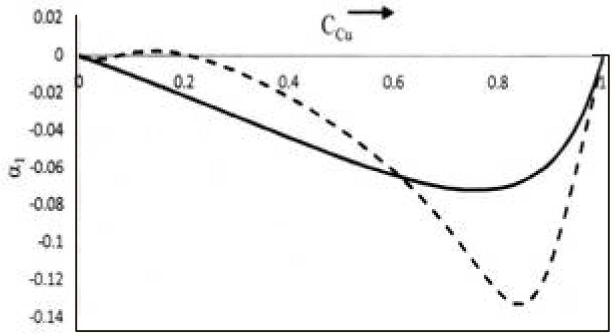

Figure 3. Concentration dependence of computed Warren-Cowley short range order parameter for Cu-Sn liquid alloys at 1500 K. The solid line represents WSE while the dashes represent NSE.

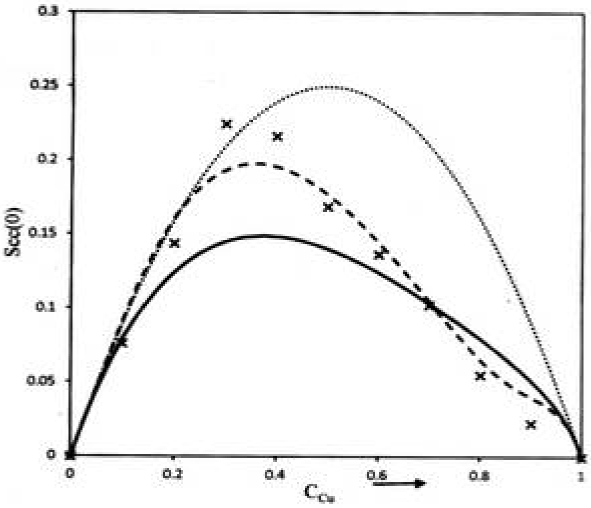

Figure 2. Concentration dependence of Scc(0) for Cu-sin at 1400 K. The solid line represents WSE while the dashes represent NSE. The times represent experimental data obtained from experimental GM/RT taken from [15]. The dots represent the ideal values.

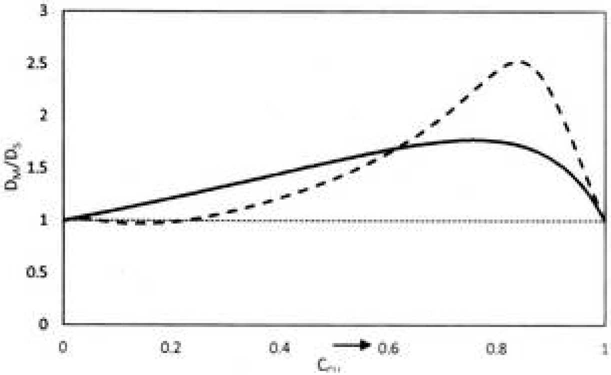

Figure 4. Concentration dependence of diffusivity of Cu-Sn liquid alloys at 1400 K. The solid line represents WSE while the dashes represent NSE.

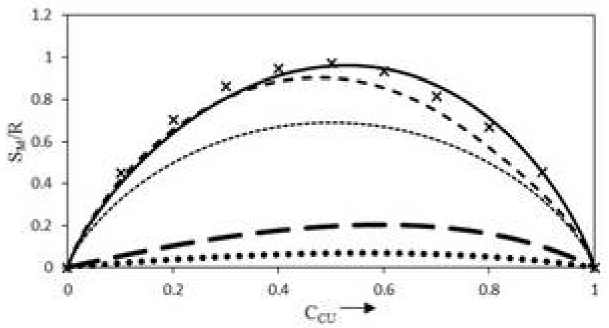

Figure 5. Concentration dependence of S_M/R for Cu-Sn liquid alloys at 1400 K. The solid line represents WSE while the dashes represent NSE. The light dots and thick dots represent the ideal values and size factor contributions to Sm, respectively. The thick dashes represent the contribution of temperature derivative of the interchange energy to S_M while the times represent the experimental values of S_M taken from [15]

C_{Cu} = 0.59 and 1.1441 in WSE (i.e. Flory's model) at C_{Cu} = 0.54) is quite less than the 3.0 criterion for evidence of strong association between the two species of atoms in a binary liquid [29]. Thus, the atomic interactions between the atoms in Cu-Sn liquid alloys are weak. This is in agreement with the reported observation of [6]. However, the result of Flory's model indicates that the atomic interactions are not as weak as indicated in CFM in the range $C_{Cu} \leq 0.75$.

Figure 2 shows that the result from CFM (i.e. NSE plot) indicates that in the composition range $0.08 \leq C_{cu} \leq 0.21$, there is evidence of homocoordination in Cu-Sn liquid alloys (i.e. Scc(0) > Scc(0,id)) while in the rest of Cu composition in Cu-Sn, there is evidence of heterocoordination in Cu-Sn liquid alloys (i.e. Scc(0) < Scc(0,id)). The result from Flory's model (i.e. WSE plot) indicates that there is evidence of heterocoordination in the entire composition of Cu in Cu-Sn liquid alloys (this is similar to the findings of Adhikari *et.al.* in Ref. [6]). Thus, the transition from order to disorder indicated by the experimental data is corroborated by the CFM while the Flory's model only shows the chemical ordering in Cu-Sn liquid alloys (as was shown in [6]). A comparison of the Scc(0) of the two models with the Scc(0,id) shows that the degree of chemical ordering in Cu-Sn liquid alloys is weak (in agreement with the reports in [6, 10, 16] but the result from Flory's model shows further that the degree of chemical ordering is not as weak as observed in the result from CFM. Also, since it has been reported that the position of maximum deviation $S_{cc}(0) - S_{cc}(0, id)$ can be used as an indicator of the possible stoichiometric composition of the chemical clusters present in the liquid phase in a binary alloy [16, 30], we observed that this maximum deviation is at C_{Cu} = 0.7, using CFM (i.e. NSE plot) and at C_{Cu} = 0.6, using Flory's model (i.e. WSE plot). This indicates that the result from CFM has a better agreement with the assumed complex Cu_3Sn in Cu-Sn liquid phase than the result from Flory's model.

In Figure 3, we observed that in the entire composition of Cu in Cu-Sn liquid alloys, the isotherm of α_1 from Flory's model (i.e. WSE plot) shows that there is weak tendency for chemical ordering in Cu-Sn liquid alloys since the value of $\alpha_1^{\min}$ is -0.07184 which is much less than $\alpha_1^{\min} = -1$ criterion for complete chemical ordering. The isotherm of α_1 from CFM (i.e. NSE plot) corroborates the earlier observation in Scc(0) that in the composition range $0.08 \leq C_{cu} \leq 0.21$, there is evidence of homocoordination in Cu-Sn liquid alloys (i.e. α_1>0) while in the rest of Cu composition in Cu-Sn, there is evidence of heterocoordination in Cu-Sn liquid alloys (i.e. α_1<0). Also, the position of the $\alpha_1^{\min}$ is at C_{Cu} = 0.84 in the isotherm NSE (i.e. CFM) while is at C_{Cu} = 0.76 in the isotherm WSE (i.e. Flory's model). This implies that the position of $\alpha_1^{\min}$ for Cu-Sn in Flory's model agree better with the assumed complex Cu_3Sn in Cu-Sn liquid phase than the result from CFM.

Figure 4 shows the result from Flory's model (i.e. WSE) which reveals that in the entire composition of Cu in Cu-Sn liquid alloys, there is a weak tendency for heterocoordination in Cu-Sn liquid alloys.This is because, although, D_M/D_S> 1 in the entire composition, its maximum magnitude of 2.0360 at C_{Cu} = 0.74 is quite lower than that of known weak interacting liquid alloy such as Al-Co whose maximum magnitude of $D_M/D_S \approx 4.8860$, as reported in [14] and strongly interacting liquid alloy like K-Sb, whose maximum magnitude of $D_M/D_S \approx 15.0$, as reported in [31]. The isotherm of D_M/D_S of Cu-Sn liquid alloys in Figure 4 obtained from CFM (i.e. NSE plot) further corroborate the earlier observations in Scc(0) and α_1 that in the composition range $0.08 \leq C_{cu} \leq 0.21$, there is evidence of homocoordination in Cu-Sn liquid alloys (i.e. D_M/D_S<1) while in the rest of Cu composition in Cu-Sn, there is evidence of heterocoordination in Cu-Sn liquid alloys (i.e. D_M/D_S>1). Also, although, its maximum magnitude of 2.5281 at C_{Cu} = 0.84 is lower than that of known strongly interacting liquid alloys, yet it is still greater than the 2.0360 obtained from Flory's model. This is an indication that the degree of heterocoordination in Cu-Sn liquid alloys, although weak, yet it is not as weak as Flory's model indicated. Additionally, the position of maximum of D_M/D_S from CFM (at $C_{Cu} = 0.84$) and at $C_{Cu} = 0.74$ in Flory's model reveals that the result of Flory's model agree better with the assumed complex Cu_3Sn in Cu-Sn liquid phase than the result of CFM.

In Figure 5, we observed that the computed S_M obtained from Flory's model (i.e.WSE) agree with the experiment in the entire Cu composition in Cu-Sn liquid alloys while the computed S_M from CFM (i.e. NSE plot), although positive as that from Flory's model in the entire Cu composition (in agreement with the report in [5]), but only have a reasonable agreement with experiment in the composition range $C_{cu} \leq 0.04$. Since the level of agreement between the computed and the experimental S_M for Cu-Sn liquid alloys in the composition range $C_{cu} \leq 0.04$ are about the same using CFM (i.e. NSE plot) and Flory's model (i.e. WSE plot), we can then infer that size effect only has significant effect on the entropy of Cu-Sn liquid alloys in the composition range $C_{cu} \geq 0.4$.

Also, the plots of the contribution of the ideal S_M (i.e. the light dots plot in Figure 5), the contribution of the temperature derivative of the interchange energy to the S_M (i.e. the thick dashes plot in Figure 5) and the contribution of the size factor to S_M (i.e. the thick dots in Figure 5) made it obvious that each of these contributions significantly contributed positively to the S_M of Cu-Sn liquid alloys at 1400 K. This is unlike in NaCs where the contributions of the temperature derivative of the interchange energy and the size factor to S_M almost cancelled each other, leaving the ideal S_M as the major and significant factor that contributed to the S_M of NaCs [24]. Also, it is worth noting that, as was the case in NaCs [24], the result of S_M for Cu-Sn liquid alloys in this figure confirmed that the contribution of the fourth term on the right hand side of Eq.(31), which contains the temperature derivative of the size factor to S_M, is quite insignificant (possibly, because $\frac{\partial B}{\partial T} = 0$). Thus, as earlier suggested by Singh and Bhatia in [24], for all practical purposes, the fourth term on the right hand side of Eq. 31, which contains the temperature derivative of the size factor to S_M, may be neglected in the computation of S_M of binary liquid alloys.

Conclusion

The effect of size difference on the bulk properties of Cu-Sn liquid alloys at 1400 K has been analysed using CFM and Flory's approximate model. The results of our investigation show that

(a) although the two models quite indicate that the atomic interactions in Cu-Sn liquid alloys at 1400 K are quite weak, Flory's model which incorporate size factor, however, further indicate that the weak interactions are not as weak as described by CFM in the range $C_{cu} \leq 0.75$. This implies that in this region of Cu composition, the atomic interactions are stronger than it had been reported in earlier study where CFM have been used.

(b) the Flory's model shows that the tendency for heterocoordination exhibited by Cu-Sn liquid alloys at 1400 K in the range $0.60 \leq C_{cu} \leq 0.90$, is not as high as described by CFM. Thus, this is an indication that size effect reduces the tendency for heterocoordination in Cu-Sn liquid alloys at 1400 K in this Cu-rich region and this reduction was neither noticed nor reported in earlier study in where CFM was used.

(c) the effect of size difference on the magnitude of integral of entropy of mixing of Cu-Sn liquid alloys at 1400 K is quite significant in the range $C_{cu} \geq 03$. Also, both size factor, ideal entropy of mixing and the temperature derivative of interchange energy contributed positively to the magnitude of integral entropy of mixing of Cu-Sn liquid alloys at 1400 K.

(d) the transition from order to disorder feature exhibited by Cu-Sn liquid alloys at 1400 K which the available experimental enthalpy of mixing from Ref. [15] indicated was consistently observed in the results from CFM. However, that this transition was never observed in any of the results from Flory's model, just as it was never observed in the results of similar properties in [16], suggests one of the following:

    i. that Flory's approximate model requires some modifications, which will possibly include reflecting complex formation in the liquid state. On this, we conjecture that incorporation of complex formation in Flory's model will improve the quality of the results from this model.

    ii. that size difference is not responsible for the order-disorder transition feature exhibited by Cu-Sn liquid alloys at 1400 K.

Since thermodynamic data have been known to be of great importance for 1) accurate calculation of phase diagrams, 2) the development of a lead-free solder database, 3) the design of new lead-free solders, and 4) the prediction of physical and chemical properties of lead-free solders [32], we are of the opinion that this research work will complement the on-going development of lead-free solders (Cu-Sn has been identified as one of the main components of this group[32]) and will also improve other industrial processes involving the use of Cu-Sn liquid alloys.

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