

Investigation on Compound Formation in Mg-Sb and Cu-Sb Liquid Alloys

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Abstract

The occurrence of compound formation in Mg-Sb and Cu-Sb liquid alloys has been discussed through investigation of concentration-dependent thermodynamic and microscopic functions such as Gibbs free energy of mixing, G_M/RT , concentration-concentration fluctuations in the long wavelength, $S_{cc}(0)$, Warren-Cowley short range order, α_l and chemical diffusion. Using the compound formation model, results suggest that Mg_3Sb_2 and Cu_2Sb compounds are formed in Mg-Sb and Cu-Sb systems respectively. It is also observed that the tendency for compound formation is greater in Mg-Sb than Cu-Sb system.

Keywords

Compound Formation Model, Heterocoordination, Mg-Sb, Cu-Sb, Gibbs Free Energy, Concentration-Concentration Fluctuations

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1. Introduction

A number of compound-formation models have been developed by theoreticians and metallurgists to understand the temperature and concentration dependence of thermodynamic and structural properties of compound-forming binary liquid alloys [1-5]. All the theoretical models have been able to recognize the fact that interaction between component elements or atoms of the alloy is the most important factor responsible for compound formation. In this paper, a statistical mechanical model based on compound formation is used to study the thermodynamic properties and microscopic functions of Mg-Sb and Cu-Sb liquid alloys at temperatures 1073 K and 1190 K respectively. This model is otherwise known as compound formation model (CFM) in weak interaction approximation [5] and has been extensively used by a number of authors to understand the alloying behavior of compound-forming alloys in refs. [5-12]. The suitability of the model for Mg-Sb and Cu-Sb can be

attributed to the symmetry of the mixing properties of both alloys about equiatomic concentration and also, the thermodynamic data obtained from experiments coupled with atomic size mismatch which are criteria for compound-forming alloy [13, 14]. In the CFM, it is assumed that the alloy AB consists of a number of A atoms, B atoms and a number of chemical complexes $A_\mu B_\nu$ ($\mu A + \nu B \rightleftharpoons A_\mu B_\nu$, μ and ν are small integers) all in chemical equilibrium with each other. This study will provide information on heterocoordination (short-range ordering) which is preference of unlike atoms to pair with nearest neighbours and a tendency of compound formation in the alloys. The interest in the theoretical study of the energetics and its effects on the alloying behavior of Mg-Sb and Cu-Sb is stemmed from the understanding that

1. Mg-Sb liquid metal battery is rapidly becoming an alternative to Li-Pb batteries for stationary energy storage

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[17].

2. The Cu-Sb system is now being used as an alternative material in perovskite solar cells [18].

The key theory supporting the calculation of thermodynamic properties and microscopic functions using the CFM model for compound forming alloys is presented in the next section. This is followed by the presentation of the results obtained and the discussion of the results in section 3. A summary of our work is presented in section 4 as a conclusion.

$$G_M^{es} = ZNK_B T \left[\left(\frac{W}{ZK_B T} \right) C(1-C) + \left(\frac{W_{AB}}{ZK_B T} \right) \phi_{AB} + \left(\frac{W_{AA}}{ZK_B T} \right) \phi_{AA} + \left(\frac{W_{BB}}{ZK_B T} \right) \phi_{BB} \right] \quad (2)$$

Where Z , N , K_B and T are coordination number, Avogadro's number, Boltzmann's constant and absolute temperature respectively. W and W_{ij} ($i, j = A, B$) are energy parameters. W is the ordering energy parameter while W_{ij} refers to energy difference of an i - j bond when one of the bond forming component (i or j) is present in the compound $A_\mu B_\nu$. ϕ_{ij} is a concentration function and its value is dependent on the choice of μ and ν . ϕ_{ij} for different set of μ and ν can be expressed in terms of C as

$$\mu = 3, \nu = 2$$

$$\phi_{AB} = \frac{13}{420}C + \frac{2}{3}C^3 - \frac{3}{2}C^4 + \frac{3}{5}C^5 + \frac{2}{3}C^6 - \frac{5}{7}C^7 + \frac{1}{4}C^8$$

$$\phi_{AA} = -\frac{53}{840}C + \frac{2}{3}C^3 - \frac{5}{4}C^4 + \frac{6}{5}C^5 - C^6 + \frac{4}{7}C^7 - \frac{1}{8}C^8 \quad (3)$$

$$\phi_{BB} = \frac{23}{280}C - \frac{1}{2}C^4 + \frac{2}{5}C^5 + \frac{1}{7}C^7 - \frac{1}{8}C^8$$

$$\mu = 2, \nu = 1$$

$$\phi_{AB} = \frac{1}{6}C + C^2 - \frac{1}{3}C^3 + \frac{1}{2}C^4$$

$$\phi_{AA} = -\frac{1}{4}C + \frac{1}{2}C^2 - \frac{1}{4}C^4 \quad (4)$$

$$\phi_{BB} = 0$$

$$S_{cc}(0) = C(1-C) \left[1 + (C(1-C))Z \left\{ \left(-\frac{2W}{ZK_B T} \right) + \left(\frac{W_{AB}}{ZK_B T} \right) \phi_{AB}'' \right\} \right]^{-1} \left\{ \left(\frac{W_{AA}}{ZK_B T} \right) \phi_{AA}'' + \left(\frac{W_{BB}}{ZK_B T} \right) \phi_{BB}'' \right\} \quad (6)$$

Where

$$\phi_{ij}'' = \frac{d^2 \phi_{ij}}{dC^2} \quad (i, j = A, B) \quad (7)$$

The ideal values of concentration-concentration fluctuations, $S_{cc}(0, id)$ corresponding to the values of $S_{cc}(0)$ when the energy parameters are zero is calculated from:

$$S_{cc}(0, id) = C(1-C) \quad (8)$$

2. Theory

2.1. Gibbs Free Energy of Mixing

In the framework of CFM, the general expression for Gibbs free energy of mixing G_M/RT is given by [5, 9]

$$G_M = G_M^{es} + [C \ln C + (1-C) \ln(1-C)] \quad (1)$$

Where G_M^{es} is the excess free energy of mixing, C is the concentration of A and $(1-C)$ is the concentration of B.

The excess free energy G_M^{es} is expressed as [9]

Eq. (1) reduces to the ideal solution (when there is no compound formation) expression when $W_{ij} = 0$. It should be noted that compound forming alloys can be grouped into two. The first group is made up of those alloys with very strong tendency for compound formation i.e. very large $\frac{W}{ZK_B T}$. The second group consists of compound forming alloy with adequately small $\frac{W}{ZK_B T}$ i.e. less than unity. Intermetallic compounds formed in his group of alloys have weaker type interaction when compared to the first group. Once the expression of G_M/RT is known, other thermodynamic functions simply follow.

2.2. Concentration-Concentration Fluctuations in the Long Wavelength Limit, $S_{cc}(0)$

$S_{cc}(0)$ is a very useful microscopic function because of its utility in understanding nature of atomic order in binary liquid alloys [20, 21]. There is a direct relationship between Gibbs free energy of mixing G_M/RT and $S_{cc}(0)$ [22-24] via the following equation

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial C^2} \right)_{T,P,N}^{-1} \quad (5)$$

Using Eqs. (2) and (5), the following expression for $S_{cc}(0)$ is obtained

Deviation of $S_{cc}(0)$ from $S_{cc}(0, id)$ provides information on the degree of interaction in a liquid binary mixture [19].

2.3. Warren-Cowley Short Range Order Parameter, α_1

A clear picture on the nature of ordering in binary liquid alloys can be obtained from the quantity α_1 [16, 22]. This parameter gives an insight to the local arrangement of atoms in the liquid alloy system. Theoretical values of α_1 are

expressed in terms of conditional probability $[A/B]$, which defines the probability of finding an A -atom as the nearest neighbor of a given B -atom. α_1 is expressed as:

$$\alpha_1 = \frac{\beta-1}{\beta+1} \quad (9)$$

Where

$$\beta = [1 + 4C(1-C)(\eta^2 - 1)]^{1/2} \quad (10)$$

Where η^2 in Eq. (10) is expressed as:

$$\eta^2 = \exp\left(\frac{2W}{ZK_B T}\right) \exp[(2P_{AB}W_{AB} - P_{AA}W_{AA} - P_{BB}W_{BB})/K_B T] \quad (11)$$

Where P_{ij} is a probability term that explains the presence of one of the component of i - j bond in chemical complex and is expressed as:

$$P_{AA} = C_A^{\mu-2} C^v (2 - C_A^{\mu-1} C_B^v), \mu \geq 2 \quad (12)$$

$$P_{BB} = C_A^\mu C_B^{v-2} (2 - C_A^\mu C_B^{v-2}), v \geq 2 \quad (13)$$

$$P_{AB} = C_A^{\mu-1} C_B^{v-1} (2 - C_A^{\mu-1} C_B^{v-1})$$

2.4. Chemical Diffusion

The alloying behavior of two molten metals can be studied at the microscopic scale in terms of diffusion. An expression that combines chemical diffusion and $S_{cc}(0)$ can be obtained by using the Darken's thermodynamic equation [23, 24]. Therefore:

$$\frac{D_m}{D_{id}} = \frac{S_{cc}(0, id)}{S_{cc}(0)} \quad (14)$$

Where D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal binary alloy given as

$$D_{id} = C D_A + (1 - C) D_B \quad (15)$$

Where D_A and D_B are self-diffusion coefficients of pure constituents A and B respectively.

3. Results and Discussion

The values of μ and v employed in this paper for both alloys are obtained from their phase diagrams [22] where their possible existence as intermetallic compounds can be seen, Mg-Sb ($\mu = 3, v = 2$) and Cu-Sb ($\mu = 2, v = 1$) at 1073 K and 1190 K respectively. The likely complexes to be formed in Mg-Sb and Cu-Sb are Mg_3Sb_2 at $C_{Cu} = 0.6$ and Cu_2Sb at $C_{Cu} = 0.7$ respectively. The value $Z = 10$ has been used for computation. The choice of Z is made from the suggestion

that Z for most liquid metallic systems could be taken as 10 after X-ray diffraction experiments reveal that atoms are in random distribution in a closed packed structure in liquid and amorphous state and the mean free path is comparable to atomic size [5, 27]. The values of the energy parameters used in this work are shown in Table 1. These values were able to reproduce to a reasonable extent the thermodynamic experimental data of G_M/RT ($R = NK_B$ and is known as universal gas constant). Eq. 1 has been used to compute G_M/RT and Figure 1 and 2 show the results of this computation. The theory and experiment agree well for both alloys except some deviations in magnitude of $C_{Sb} = 0.6, 0.7$ and 0.8 in Mg-Sb alloy.

Table 1. Energy parameters obtained from computation of the thermodynamic properties and functions of Mg-Sb and Cu-Sb at temperatures of 1073 K and 1190 K respectively.

Alloy	T(K)	$\frac{W}{RT}$	$\frac{W_{AB}}{RT}$	$\frac{W_{AA}}{RT}$	$\frac{W_{BB}}{RT}$
Mg-Sb	1073	-15.000	-0.100	0.00	0.00
Cu-Sb	1190	-0.068	-3.880	0.00	0.00

The minimum of G_M/RT for Mg-Sb is about -4.26 while that of Cu-Sb is about -1.32. This is evidence that Mg-Sb is more heterocoordinated or strongly interacting than Cu-Sb, $\frac{G_M}{RT} \leq 3.0$ [24]. The values also indicate the tendency to form compound is very strong in Mg-Sb.

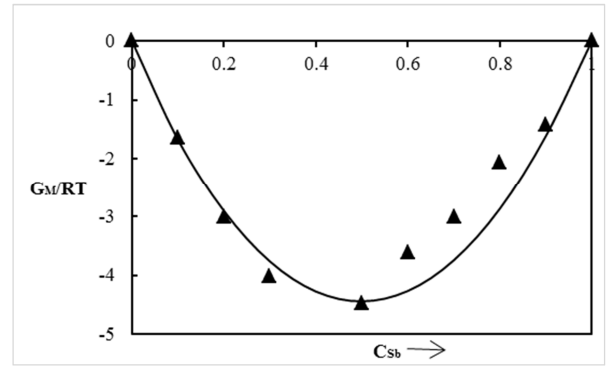


Figure 1. Concentration dependence of free energy of mixing, $\frac{G_M}{RT}$ for Mg-Sb (curve) liquid alloy at 1073 K, computed from Eq. (1). The concentration of Sb in Mg-Sb is represented as C_{Sb} . The triangles are experimental values of $\frac{G_M}{RT}$ for Mg-Sb.

In principle, $S_{cc}(0)$ can be obtained from small angle diffraction experiments, however, experimental determination of $S_{cc}(0)$ is not simple [24, 25]. Eqs. (6) and (8) have been used to compute $S_{cc}(0)$ and $S_{cc}(0, id)$ respectively. The computed values can be seen in Figure 3 and Figure 4. We have no experimental values for concentration fluctuations of Mg-Sb and Cu-Sb alloys.

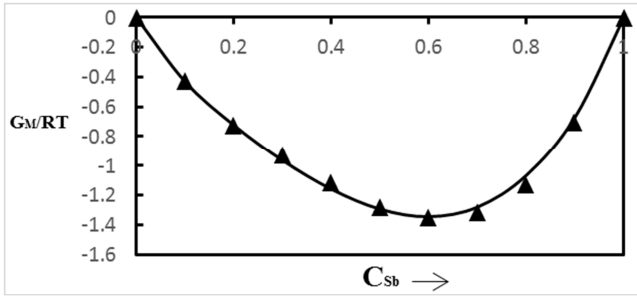


Figure 2. Concentration dependence of free energy of mixing, $\frac{G_M}{RT}$ for Cu-Sb (curve) liquid alloy at 1190 K, computed from Eq. (1). The concentration of Sb in Cu-Sb is represented as C_{Sb} . The triangles are experimental values of $\frac{G_M}{RT}$ for Cu-Sb.

$S_{cc}(0) < S_{cc}(0, id)$ at any given concentration is an evidence of heterocoordination. If $S_{cc}(0) > S_{cc}(0, id)$, then there is tendency for segregation (preference of like atoms to pair together as nearest neighbours). Heterocoordination in Mg-Sb can be observed in Figure 3 throughout the entire range of concentration indicating presence of chemical order in the alloy. In the case of Cu-Sb, theoretical investigation suggests segregation around $C_{Sb} = 0.2$. instead of compound formation.

The Warren-Cowley short range order parameter, α_1 for the two alloys has been computed using Eq. (9). The results are shown in Figures. 5 and 6. For equiatomic composition, α_1 is found to be $-1 \leq \alpha_1 \leq 1$. Negative values of α_1 indicates the presence of chemical order while its positive values indicate segregation. It should be noted that $\alpha_1^{min} = -1$ means complete order of unlike atom pairing while $\alpha_1^{min} = 1$ means phase separation.

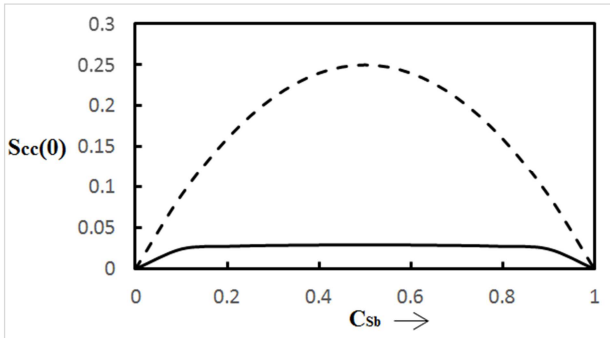


Figure 3. Concentration dependence of concentration-concentration fluctuations, $S_{cc}(0)$ for Mg-Sb (curve) alloy at 1073 K. The dashes represent the ideal values of concentration-concentration fluctuations, $S_{cc}(0, id)$. C_{Sb} is the concentration of Sb in Mg-Sb.

It can be seen from Figure 5 and 6 that α_1 has negative values across the whole concentration range in both alloys from which the presence of chemical order in both alloys may be inferred. This means that the two alloys investigated are heterocoordinated systems as evident in the computations of G_M/RT and $S_{cc}(0)$. However, the degree of order is larger in Mg-Sb alloy ($\alpha_1^{min} = -1$ at $C_{Sb} = 0.5$) than Cu-Sb ($\alpha_1^{min} = -0.707$ at $C_{Sb} = 0.5$). Also, the α_1 is symmetrical about equiatomic composition.

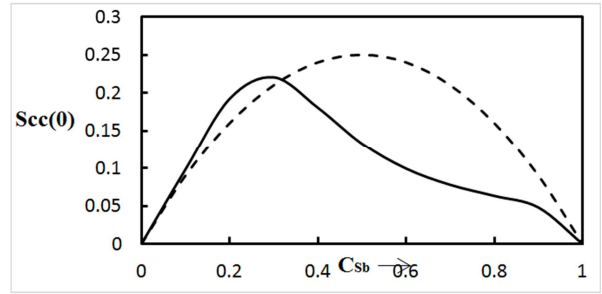


Figure 4. Concentration dependence of concentration-concentration fluctuations, $S_{cc}(0)$ for Cu-Sb (curve) alloy at 1190 K. The dashes represent the ideal values of concentration-concentration fluctuations, $S_{cc}(0, id)$. C_{Sb} is the concentration of Sb in Cu-Sb.

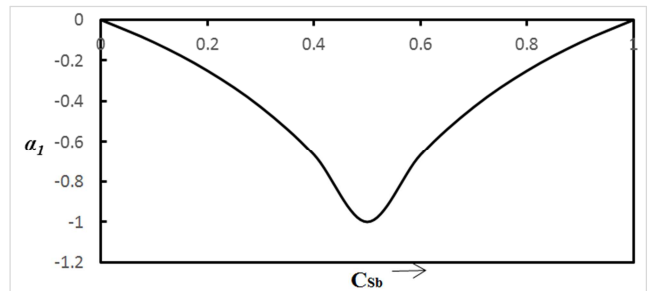


Figure 5. Concentration dependence of Warren-Cowley short range order parameter, α_1 for Mg-Sb (curve) alloy at 1073 K. C_{Sb} is the concentration of Sb in Mg-Sb.

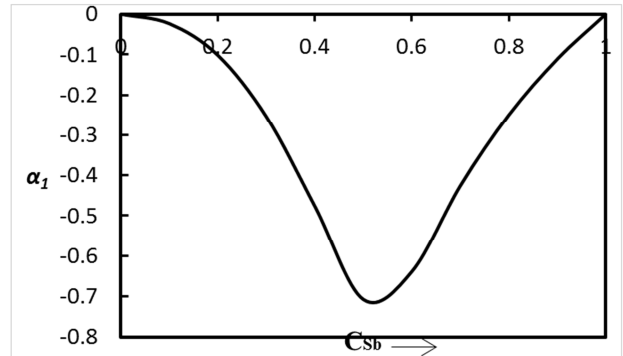


Figure 6. Concentration dependence of Warren-Cowley short range order parameter, α_1 for Cu-Sb (curve) alloy at 1190 K. C_{Sb} is the concentration of Sb in Cu-Sb.

For an ideal mixture, $D_M \rightarrow D_{id}$: for ordered alloys, $D_M > D_{id}$: and likewise for segregation for segregation, $D_M < D_{id}$. The maximum of $\frac{D_m}{D_{id}}$ indicates maximum chemical order in the alloy. The chemical diffusion coefficient, $\frac{D_m}{D_{id}}$ has been calculated as a function of concentration via Eq. (14) by using computed values of $S_{cc}(0)$ as shown in Figure 7 and 8. It is noticed that $\frac{D_m}{D_{id}}$ is greater than 1 throughout the concentration range of both alloys except in Cu-Sb where $\frac{D_m}{D_{id}}$ is less than 1 at $C_{Sb} = 0.2$. It can also be inferred from the plot of $\frac{D_m}{D_{id}}$ versus concentration that the degree of chemical order is greater in Mg-Sb than Cu-Sb.

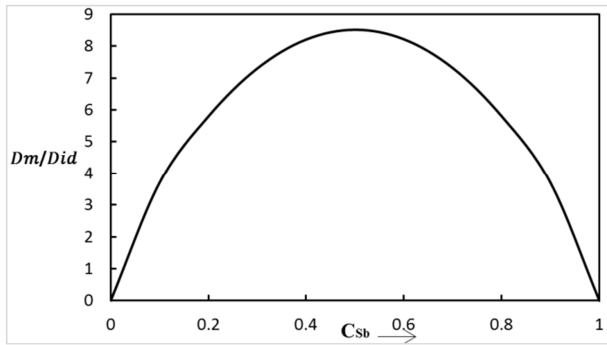


Figure 7. Concentration dependence of chemical diffusion coefficient, $\frac{D_m}{D_{id}}$ using Eq (14) Mg-Sb at 1073 K.

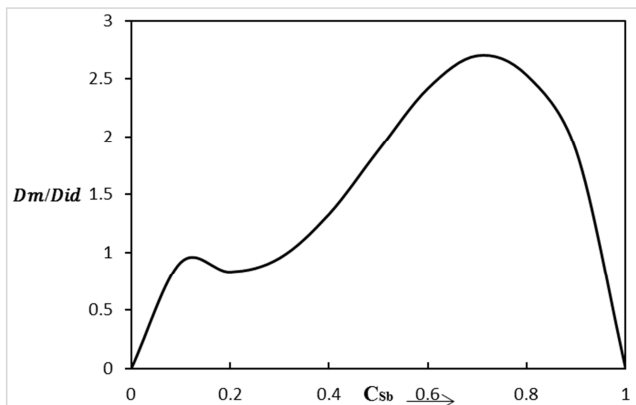


Figure 8. Concentration dependence of chemical diffusion coefficient, $\frac{D_m}{D_{id}}$ using Eq (14) Cu-Sb at 1190 K.

4. Conclusion

The theoretical study of concentration dependence of thermodynamic functions such as Gibbs free energy of mixing, concentration fluctuations, the Warren-Cowley short range order and chemical diffusion have been used to deduce nature of compound formation and chemical order in Mg-Sb and Cu-Sb molten alloys. The study reveals the tendency for compound formation in both alloys, although the tendency is greater in Mg-Sb. Also, both alloy are heterocoordinated, but Mg-Sb is more heterocoordinated throughout the entire concentration with Cu-Sb showing tendency for segregation at $C_{Sb} = 0.2$.

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