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Thermodynamics and atomic order in molten Mg-Bi alloy

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ABSTRACT

The quasi-lattice model based on pairwise interactions has been used to study the large deviation from the ideal mixture and the concentration dependent asymmetry in the thermodynamic properties of Mg-Bi liquid alloy. This has been utilised to extract microscopic information such as concentration-concentration structure factor in long wavelength limit [Scc(o)] and warren-cowley short range order parameter α_1 of Mg-Bi liquid alloy at 975K. The analysis suggests that heterocoordination leading to the formation of complex Mg_3Bi_2 is likely to exist in the melt, and is of strongly interacting nature. The theoretical analysis reveals that the pairwise interaction energies between the species depend considerably on temperature and the alloy is chemically more ordered in Mg-rich region of the phase diagram. The alloy behaves like a segregating system in Bi-rich region. Copyright © 2013 VBRI press.

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Introduction

There has been considerable interest of theoreticians to explain the concentration dependent asymmetry in the properties of mixing of binary liquid alloys and hence to extract additional microscopic information. Most of the binary alloys possess characteristic features that most of their thermodynamic properties like free energy of mixing, heat of mixing, entropy [**1**] and many other electrical properties [**2, 3**] are asymmetric as the function of concentration. Such an asymmetry is generally attributed to size effect [**4**] and the interactions between solute and solvent atoms or both. If the size effect is not large enough to be the cause of anomaly then it may be attributed [**5-8**] to the strong interactions present in it. Because of the strong interactions, these alloys form inter metallic compounds at one or more stoichiometric compositions in solid state. Large negative excess free energy of mixing G_M^{XS}, entropy of mixing (S_M), heat of mixing (H_M) with a sharp change in slope near the compound forming concentrations are the characteristics [**1, 8, 9**] of compound forming alloys. The formation of compounds in

solid state led many theoreticians [**5, 10-14**] to believe that chemical complexes, pseudomolecules and privileged group of atoms might exist in molten state. Various theoretical models [**15-18**] based on these assumptions have been used to investigate the alloying behaviours of such type of binary alloys.

The size effect ($\Omega Bi/\Omega Mg = 1.526$, where Ω is atomic volume) is too small in Mg-Bi system to exhibit the observed asymmetry; it is therefore expected that concentration dependent asymmetry arises due to energy effects. Therefore, we have used quasi-lattice model [**17, 18**] to investigate the alloying behaviour of Mg-Bi liquid alloy at 975K. Since Mg_3Bi_2 is a well-defined solid intermediate phase which melts at 975K, it is likely that such associates in same form also exist is liquid phase. The phase diagram of Mg-Bi system contains just one intermetallic compound with two eutectics on either side [**1, 19**]. The liquidus line of Mg-Bi system resembles to that Mg-Sn, however the maximum for Mg-Bi is more pronounced at stoichiometric composition.

The quasi-lattice model presumes that number μ of Mg atoms and the number υ of Bi atoms are energetically favoured to form chemical complexes:

μ Mg + υ B $\rightleftharpoons$ Mg_3Bi_2 [μ =3, υ =2]

Accordingly, the melt of Mg-Bi alloy can be assumed to consist of the mixture of left over Mg-atoms, Bi atoms and a number of chemical complexes Mg_3Bi_2, all of which are in chemical equilibrium with each-other.

On this basis we have calculated the thermodynamic quantities such as free energy of mixing, entropy of mixing and heat of mixing. To understand the atomic order of the alloy, we have calculated the concentration fluctuation in long wavelength limit [Scc(0)] and the short range order parameter α_1. The compound formation and segregation can easily be interpreted through the study of [Scc(0)] and α_1 [**20-27, 28, 29**].

In section 2 the general formulation of quasi-lattice model has been summarised to simple expression, section 3 deals with the results and discussions and section 4 provides the conclusion.

Formulation

The alloys which in solid or liquid state form a chemical compound at one or more well defined chemical composition and the complexes or the privileged group of atoms exist in molten state, the quasi-lattice model is applicable. The quasi-lattice model is statistical model in which grand partition function is used. In this model it is assumed that the energy of a given nearest neighbour bound is different if it belong to the complex than if it dies not. The model envisages the existence of chemical complex $A\mu B\upsilon$, where μ and υ are small integers, and A and B the constituent species of the alloy.

$$\mu A + \upsilon B \rightleftharpoons A\mu B\upsilon$$

With this consideration the expression for excess-free energy of mixing comes to be

$$G_M^{XS} = Nk_BT \int_0^c \ln\gamma dc \quad (1)$$

Where N is the total number of atoms in the alloy, c the concentration of A-atom, T the absolute scale temperature and k_B the Boltzman constant. If γ_A and γ_B be the activity co-efficient of atom-A and atom-B respectively then

$$\ln\gamma = \ln\left(\gamma_A/\gamma_B\right) = Z\ln\sigma + \frac{Z}{2k_BT}\left[P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}\right] + \phi \quad (2)$$

where Z is the coordination number, ϕ a constant and P_{ij} the probability that ij bond belongs to the complex and in given by

$$P_{AB} = c^{\mu-1}(1-c)^{\upsilon-1}\left[2 - c^{\mu-1}(1-c)^{\upsilon-1}\right] \quad (3)$$

where i,j = A, B

$$P_{AA} = c^{\mu-2}(1-c)^{\upsilon-1}\left[2 - c^{\mu-2}(1-c)^{\upsilon}\right] \text{ for } \mu \geq 2 \quad (4)$$

$$P_{BB} = c^{\mu}(1-c)^{\upsilon-1}\left[2 - c^{\mu}(1-c)^{\upsilon-2}\right] \text{ for } \upsilon \geq 2 \quad (5)$$

P_{AA} and P_{BB} are zero for $\mu<2$ and $\upsilon<2$ respectively, ε_{ij} denotes the energy of ij bond if it is a free bond and (ε + $\Delta\varepsilon_{ij}$) its energy if it is one of the bond in complex $A\mu B\upsilon$. The term σ of right hand side in equation (2) is given by

$$\ln\sigma = \frac{1}{2}\ln\frac{(1-c)\theta + 2c - 1}{c\theta - 2c + 1} \quad (6)$$

where $\theta = \sqrt{1 + 4c(1-c)(\eta^2 - 1)}$ (7)

$$\eta^2 = \exp\left(\frac{2\omega}{Zk_BT}\right)\exp\left(\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{k_BT}\right) \quad (8)$$

where $\omega = Z\left(\varepsilon_{AB} - \frac{1}{2}\varepsilon_{AA} - \frac{1}{2}\varepsilon_{BB}\right)$ (9)

and is known as ordering energy.

The constant ϕ appearing in equation (2) can now be determined by setting

$$\int_0^1 \ln\gamma dc = 0 \quad (10)$$

It however depends upon the values of μ and υ. Using equation (3), (4) and (5) we obtain

$$\begin{aligned} k_BT\phi = {} & \Delta\omega_{AB}\left[2\beta(\mu+1,\upsilon) - 2\beta(\mu,\upsilon+1) + \beta(2\mu-1,2\upsilon) - \beta(2\mu,2\upsilon-1)\right] \\ & + \Delta\omega_{AA}\left[\beta(2\mu-2,2\upsilon+1) - 2\beta(\mu,\upsilon+1)\right] \\ & + \Delta\omega_{BB}\left[2\beta(\mu+1,\upsilon) - \beta(2\mu+1,2\upsilon-2)\right] \end{aligned} \quad (11)$$

Where, $\beta(\mu,\upsilon) = \beta(\upsilon,\mu) = \int_0^c c^{\mu-1}(1-c)^{\upsilon-1}dc = \frac{\Gamma(\mu)\Gamma(\upsilon)}{\Gamma(\mu+\upsilon)}$ (12)

Here, for convenience we have introduced,

$$\Delta\omega_{ij} = Z\Delta\varepsilon_{ij} \quad (13)$$

It is understood from equations (4) and (5) that in equation (11) $\Delta\omega_{AA}$ is identically zero if μ=1 and $\Delta\omega_{BB}$ is also zero if υ=1.

In association with the above relations we get from equation (1) a closed form expression for the excess free energy of mixing.

$$G_M^{XS} = N[c(1-c)\omega + \phi_{AB}\Delta\omega_{AB} + \phi_{AA}\Delta\omega_{AA} + \phi_{BB}\Delta\omega_{BB}] \quad (14)$$

ϕ_{ij}'s can be expressed explicitly in terms of c for given values of μ and υ. In case of magnesium-bismuth liquid alloy A=Mg, B=Bi, μ=3, ν=2.

$$\phi_{AB}(c) = \frac{13}{420}c + \frac{2}{3}c^3 - \frac{3}{2}c^4 + \frac{3}{5}c^5 + \frac{2}{3}c^6 - \frac{5}{7}c^7 + \frac{1}{4}c^8 \quad (15)$$

$$\phi_{AA}(c) = -\frac{53}{840}c + \frac{2}{3}c^3 - \frac{5}{4}c^4 + \frac{6}{5}c^5 - c^6 + \frac{4}{7}c^7 + \frac{1}{8}c^8 \quad (16)$$

$$\phi_{BB}(c) = \frac{23}{280}c - \frac{1}{2}c^4 + \frac{2}{5}c^5 + \frac{1}{7}c^7 - \frac{1}{8}c^8 \quad (17)$$

Using equations (15), (16), (17) and (14)

$$G_M^{xs} = N\left[\omega c(1-c) + \Delta\omega_{AB}\left(\frac{13}{420}c + \frac{2}{3}c^3 - \frac{3}{2}c^4 + \frac{3}{5}c^5 + \frac{2}{3}c^6 - \frac{5}{7}c^7 + \frac{1}{4}c^8\right)\right.$$
$$+ \Delta\omega_{AA}\left(-\frac{53}{840}c + \frac{2}{3}c^3 - \frac{5}{4}c^4 + \frac{6}{5}c^5 - c^6 + \frac{4}{7}c^7 - \frac{1}{8}c^8\right)$$
$$\left. + \Delta\omega_{BB}\left(\frac{23}{280}c - \frac{1}{2}c^4 + \frac{2}{5}c^5 + \frac{1}{7}c^7 - \frac{1}{8}c^8\right)\right] \quad (18)$$

The free energy of mixing for binary alloys

$G_M = G_M^{xs} + RT\,[c\ln c + (1-c)\ln(1-c)]$ ..... (19)

where R is universal gas constant.

The excess entropy of mixing is given by

$$S_M^{xs} = -\left(\frac{\partial G_M^{xs}}{\partial T}\right)_p \quad (20)$$

Using equations (18) and (20) we obtain

$$S_M^{xs} = -N\left[\frac{\partial\omega}{\partial T}\phi(c) + \frac{\partial(\Delta\omega_{AB})}{\partial T}\phi_{AB}(c) + \frac{\partial(\Delta\omega_{AA})}{\partial T}\phi_{AA}(c) + \frac{\partial(\Delta\omega_{BB})}{\partial T}\phi_{BB}(c)\right] \quad (21)$$

where, $\phi(c) = c(1-c)$ (22)

So, the entropy of mixing for such a binary alloy

$S_M = S_M^{xs} - R\,[c\ln c + (1-c)\ln(1-c)]$ (23)

Now, the heat of mixing can be found out using equations (19) and (23) from standard thermodynamic relation,

$H_M = G_M + TS_M$ (24)

To understand the atomic order in binary liquid alloy it is instructive to study the behavior of the long wavelength limit of the concentration-concentration structure factor [Scc(0)] given as.

$Scc(0) = Nk_BT\,(\partial^2 G_M/\partial c^2)^{-1}_{T,P,N}$ (25)

Using equations (18), (19) and (24), we obtain,

$$Scc(0) = \frac{c(1-c)}{1 + \frac{c(1-c)}{k_BT}\left[-2\omega + \Delta\omega_{AB}\phi''_{AB} + \Delta\omega_{AA}\phi''_{AA} + \Delta\omega_{BB}\phi''_{BB}\right]} \quad (26)$$

where $\phi''_{ij} = \frac{\partial^2\phi_{ij}}{\partial C^2}$ (27)

The experimental determination of Scc(0) poses more difficulty but it can be determined from measured activity data and is treated as experimental values given as

$$Scc(0) = (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = ca_B\left(\frac{\partial a_B}{\partial c}\right)^{-1}_{T,P,N} \quad (28)$$

where a_A and a_B are activities of species A and B respectively.

The Warren-Cowley short range order parameter (α_1) can be estimated from the knowledge of Scc(0) as

$$\alpha_1 = \frac{(S-1)}{S(Z-1)+1} \quad (29)$$

where, $S = \frac{Scc(0)}{S^{id}cc(0)}$ (30)

$$Scc(0)^{id} = c(1-c) \quad (31)$$

where Z is co-ordination number. In present calculation we have taken Z=10

Results and discussion

Free energy of mixing

For the computation of free energy of mixing $\left(G_M/RT\right)$ of molten Mg-Bi alloy as a function of concentration at 975K from equations (18) and (19) energy parameters ω, ω_{AB}, ω_{AA} and ω_{BB} are required. These parameters were determined from experimental values of G_M [**1**] in the concentration range of c_{Mg}=0.1 to c_{Mg}=0.9 by the method of successive approximation. The best fit parameters were found to be

$$\omega/K_BT = -8.25,\ \frac{\Delta\omega_{AB}}{K_BT} = -6.5,\ \frac{\Delta\omega_{AA}}{K_BT} = -51.0 \text{ and } \frac{\Delta\omega_{BB}}{K_BT} = -5.2$$

All the interaction energies have large negative values, showing that Mg and Bi atoms are attracted to each other and also to the complex.

The theoretical and experimental values of free energy of mixing G_M/RT are plotted in the concentration rang C_{Mg} = 0.1 to C_{Mg} =0.9. The theoretical results are in good agreement with the experimental values. Both the theoretical and experimental values are negative at all concentrations. Both show minimum at C_{Mg}=0.556, which is very close to stoichiometric composition $c_c = \frac{\mu}{\mu+\upsilon}$.

The theoretical minimum value of G_M is $\left(G_M^{min} = -3.262\,RT\right)$, while experimental minimum value is $\left(G_M^{min} = -3.390\,RT\right)$. The calculated and observe values of free energy of mixing suggest that Mg-Bi is a strongly interacting system similar to liquid amalgams such as Hg-K $\left(G_M^{min} = -3.3464RT\right)$and Hg-Na $\left(G_M^{min} = -3.1278RT\right)$.

Entropy of mixing

To determine the entropy of mixing (S_M) Using equations (21), (22) and (23) we need temperature derivatives of energy parameters. The observed values of excess entropy

of mixing [**1**] were utilized to obtain the temperature derivatives by the successive approximation. The best fit parameters were found to be

$$\frac{1}{k_B}\frac{\partial\omega}{\partial T}=-1,\quad \frac{1}{k_B}\frac{\partial(\Delta\omega_{AB})}{\partial T}=+3.5,\quad \frac{1}{k_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}=-0.8\quad \text{and}\quad \frac{1}{k_B}\frac{\partial\Delta\omega_{BB}}{\partial T}=+4.2$$

The theoretical and experimental values of S_M/R against c_{Mg} are plotted. The theoretical and experimental values are in reasonable agreement with some discrepancies. The experimental value $\left(S_M/R=0.780\right)$ shows maximum value at c_{Mg}=0.5, While the theoretical value shows maximum $\left(S_M/R=0.742\right)$ at c_{Mg} = 0.556. Both the theoretical and experimental values of S_M/R show depressions at c_{Mg}= 0.556 at c_{Mg}= 0.68 which indicate phase boundaries [**1**].

Heat of mixing

Heat of mixing (H_M) has been calculated from equation (24) using the same inter action parameters $\omega,\Delta\omega_{AA}$ and $\Delta\omega_{BB}$ and their temperature derivatives $\frac{1}{K_B}\frac{\partial\omega}{\partial T},\frac{1}{K_B}\frac{\partial(\Delta\omega_{AB})}{\partial T},\frac{1}{K_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}$ and $\frac{1}{K_B}\frac{\partial(\Delta\omega_{BB})}{\partial T}$ as used in computing G_M and S_M. The plot of H_M/RT versus c_{Mg} at 975K is depicted. Like the experimental values [**1**], H_M is negative at all concentrations. There is a reasonable agreement between theory and experiment. The minimum of H_M/RT is observed around c_{Mg}=0.6, which corresponds to stoichiometric concentration or compound formation composition. It is interesting to observe that concentration dependent asymmetry is H_M as observed from the experiment can be explained if one considers the temperature dependence of energy parameters for Mg-Bi liquid alloy.

Concentration-concentration structure factor in long wavelength limit [Scc(0)] and short ranges order parameter (α_l)

The concentration fluctuation in long wavelength limit [Scc(0)] has emerged as a very useful thermodynamic parameter to investigate the atomic order in a binary liquid alloy. While discussing [Scc(0)], it is instructive to mention its characteristic features. The deviation of Scc(0) from the ideal values $\left[S^{id}cc(0)=c_Ac_B\right]$ can be used to visualise the nature of atomic order and the stability of the mixture at a given composition. If at a given composition, $Scc(0)>S^{id}cc(0)$, there is a tendency of segregation. On the other hand, $Scc(0)<S^{id}cc(0)$ refers to heterocoordination.

The theoretical values of Scc(0) were computed from equation (26) using the same interaction parameters used to calculate G_M. The theoretical and experimental values are depicted. The theoretical values are in reasonable agreement with experimental values calculated from activity data. The experimental curve shows minimum at c_{Mg}=0.6, but the theoretical curve shows minimum at c_{Mg}=0.7. Our theoretical investigation shows that $Scc(0)>S^{id}cc(0)$ in the concentration range $0.15\le c_{Mg}\le 0.25$, suggesting that Mg-Bi system is segregating in this region. But in the concentration range $c_{Mg}>0.25$, $Scc(0)<S^{id}cc(0)$, and is quite asymmetric around equiatomic composition. That is to say that order (preference for unlike atoms to be paired as nearest neighbors) exists in the molten alloy of Mg-Bi system in this region. It is to be noted that the experimental value of Scc(0) also shows segregation in lower concentration of c_{Mg} and in higher concentration region the alloy is ordered.

In order to quantify the degree of ordering, we have calculated the warren-cowley short range order parameter α_1 for Mg-Bi liquid alloy. Experimentally α_1 can be determined from concentration-concentration structure factor $S_{cc}(q)$ and number-number structure factor $S_{NN}(q)$. However it is difficult in practice to determine $S_{cc}(q)$ and $S_{NN}(q)$ for all kinds of binary liquid alloys [**30, 31**]. Fortunately the only experimental value [**5, 32**] available for Mg-Bi system is α_1=-0.44 at c_{Mg} = 0.7. On the other hand α_1 can be evaluated theoretically from the knowledge of Scc(0) using equations (29) and (30). α_1 provides immediate insight into the local arrangements of the atoms in the mixture. Essentially negative values of α_1, can be interpreted as evidence of unlike atom pairing as nearest neighbours or compound formation. α_1=0, corresponds to random distribution and α_1>0 corresponds to like atoms pairing as nearest neighbours in first coordination shell or segregation.

The computed values of α_1 as a function of concentration are plotted. The positive value of α_1 in the concentration range $0.15\le C_{Mg}\le 0.25$ suggests that Mg-Bi system is segregating system in this range of concentration. In the concentration range $c_{Mg}>0.25$, α_1 is negative showing that Mg-Bi system is an ordered system in this range of concentration. The minimum value of α_1 occurs at c_{Mg} =0.68 [α_1=-0.432], and at c_{Mg} = 0.7, α_1=-0.428 is well within the bounds of experimental value, α_1= -0.44 [**5, 32**]. The asymmetry in α_1 is distinctly visible. We observe that Mg-rich end of phase diagram is more ordered than Bi-rich end.

Conclusion

In the present work, quasi-lattice model has been used to study the concentration dependent asymmetry of thermodynamic properties and ordering phenomena in Mg-Bi molten alloys. From our calculations Mg-Bi liquid

alloy exhibit marked deviation from ideal solutions behaviors. The concentration dependent asymmetry can be successfully produced by considering the existence of heterocoordinated complexes Mg_3Bi_2 in the molten phase. The concentration fluctuation shows Mg-Bi as slightly segregating in concentration range $0.15 \le C_{Mg} \le 0.25$, and an ordering system of unlike atoms in the concentration range $c_{Mg} > 0.25$ which is almost complete for $c_{Mg}=0.7$. This could be explained on the basis that the formation of the complex Mg_3Bi_2 is of a strong nature in the molten phase. The positive value of α_1 in concentration range $0.15 \le c_{Mg} \le 0.25$ also supports its segregating nature in this region. The computed value of $\alpha_1 = -0.428$ at $c_{Mg}=0.7$ is well within the bounds of only available experimental value $\alpha_1 = -0.44$ at $c_{Mg}=0.7$. The theoretical analysis also suggests that most of the energy parameters of Mg-Bi are strongly temperature dependents.

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