Thermodynamic and structural properties of Mg-Tl liquid alloy

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Abstract

The concentration dependent asymmetry in mixing properties of Mg-Tl liquid alloys at 923 K has been investigated on the basis of regular associated solution model. The concentration of ApB type complex in a regular associated solution of Mg and Tl have been determined. We have then used the concentration of complex to calculate the free energy of mixing, enthalpy of mixing, entropy of mixing, activity, concentration fluctuations in long wavelength limit $S_{CC}(0)$ and the Warren Cowley short-range parameter α_1 .The analysis suggests that heterocoordination leading to the formation of chemical complex Mg_2Tl is likely to exist in the melt. The analysis reveals that there is a tendency of unlike atom pairing (Mg-Tl) in Mg-Tl alloy whole range of concentration.

1. Introduction

Physics and chemistry of liquid alloys, in which the atomic arrangement is not spatially periodic in contrast to the case of crystalline materials, is well-recognized as important and promising area for research. Structural and thermodynamic properties of the initial melt play important role in the formation of alloy. Thus the properties of alloys in the melt are helpful to understand the alloying behaviour of alloys in solid state.

Growing technological interest to the nonperiodicity in the atomic arrangement of disordered materials has led to an increasing need for a better description of their atomic scale structures. In this paper, we intend to study the thermodynamic properties of Mg-Tl alloys in liquid state at 923 K on the basis of regular associated solution model. In regular associated solution model strong interaction among the constituent species of the alloy is assumed [1-5]. Such assumptions have been used in different models [6-10] by the investigators.

The phase diagram of Mg-Tl alloys shows the existence of Mg-Tl and Mg_2Tl intermetallic compounds in its solid state [11].In this paper; we have assumed Mg_2Tl complex is energetically favoured in the liquid state of Mg-Tl alloy. Assuming Mg_2Tl complex, we have determined free

energy of mixing (G_M), heat of mixing (H_M), entropy of mixing (S_M), concentration fluctuation in long wavelength limit ($S_{CC}(0)$) and chemical short range order parameter (α_1) of Mg-Tl liquid alloy at 923 K. Basic formalism of regular associated solution model is given in Section 2 and Section 3 deals with the numerical results and discussion. Conclusion is provided in section 4.

2. Basic Formalism

Let us consider one mole of binary solution comprising of x_1 mole of A atoms and x_2 moles of B atoms. The presence of ApB type complex in the solution results in a depletion of concentration of free atoms of the components of A and B. The liquid solution is thus composed of three species namely free atoms A and B and the complex ApB. As a result of associations, the thermodynamic behaviour of the components A and B is governed by the true mole fractions x_A and x_B rather than the gross mole fraction x_1 and x_2. Thus it is convenient to operate with two frames of references, one referring to gross mole fractions x_1 and x_2 and other referring to actual mole fractions of each species (x_A, x_B and x_{ApB}). Further, it is assumed that there are n_1 moles of species A, n_2 moles of species B and n_3 moles of species ApB per mole of the binary solution. From the conservation of mass, the two frames of reference can be interrelated as follows:

$$n_1 = x_1 - pn_3$$
$$n_2 = x_2 - n_3$$

and
$$n = n_1 + n_2 + n_3 = 1 - pn_3 \tag{1}$$

$$x_A = \frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{1 - pn_3}$$

$$x_B = \frac{n_2}{n_1 + n_2 + n_3} = \frac{n_2}{1 - pn_3}$$

and

$$x_{ApB} = \frac{n_3}{n_1 + n_2 + n_3} = \frac{n_3}{1 - pn_3} \tag{2}$$

Here,

$$\frac{1}{n} = \frac{1}{1 - pn_3} = 1 + \frac{pn_3}{1 - pn_3} = 1 + px_{ApB} \tag{3}$$

Now using Eq. (2.3) in Eq. (2.2), we have,

$$n_1 = \frac{x_A}{1 + px_{ApB}}, \quad n_2 = \frac{x_B}{1 + px_{ApB}}, \quad n_3 = \frac{x_{ApB}}{1 + px_{ApB}} \tag{4}$$

For the sake of convenience one or more of these frames of reference may be used.
Now x_A, x_B and x_{ApB} can be inter-related with each other as follows
$$x_1 x_2 = x_2 x_1$$

Using $n_1 = x_1 - pn_3$ and $n_2 = x_2 - n_3$, we get

$$(n_1 + pn_3)x_2 = (n_2 + n_3)x_1$$

After performing some algebraic operations and rearranging the terms, we obtain

$$n_1(x_1 + x_2) + px_2 n_3 = x_1(n_1 + n_2 + n_3)$$

and

$$x_A = x_1 - px_2 x_{ApB} \tag{5a}$$

Similarly we can obtain

$$x_B = x_2 - (1 - px_2)x_{ApB} \tag{5b}$$

The equilibrium constant for the reaction $ApB \Leftrightarrow pA + B$ is given

$$k = \frac{x_A^p x_B \gamma_A^p \gamma_B}{x_{ApB} \gamma_{ApB}} \tag{6}$$

where γ_A, γ_B and γ_{ApB} are activity coefficients of monomers A, B and complex ApB.

Following Lele and Ramchandrarao [1] the free energy of mixing G_M is given by

$$G_M = \frac{1}{(1 + px_{ApB})}(x_A x_B \omega_{12} + x_A x_{ApB}\omega_{13} + x_B x_{ApB}\omega_{23}) + \frac{RT}{(1 + px_{ApB})} \times$$

$$(x_A \ln x_A + x_B \ln x_B + x_{ApB} \ln x_{ApB}) + \frac{x_{ApB}}{(1 + px_{ApB})} RT \ln k$$

$$\tag{7}$$

where ω_{12}, ω_{13} and ω_{23} are interaction energies for the species A, B ; A, A$_p$B and B, A$_p$B respectively, T the temperature and R stands for the universal gas constant.

Progonine and Defay [12] have shown that in associated solutions, the gross chemical potentials of components 1 and 2 are equal to the chemical potentials of the monomeric species A and B. Following Jordan [2] the activity coefficients γ_A, γ_B and γ_{ApB} of monomers and complex can be expressed in terms of pairwise interaction energies through

$$RT \ln \gamma_A = x_B^2 \omega_{12} + x_{ApB}^2 \omega_{13} + x_B x_{ApB}(\omega_{12} - \omega_{23} + \omega_{13}) \tag{8a}$$

$$RT \ln \gamma_B = x_{ApB}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{ApB}(\omega_{23} - \omega_{13} + \omega_{12}) \tag{8b}$$

$$RT \ln \gamma_{ApB} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_B x_B(\omega_{13} - \omega_{12} + \omega_{23}) \tag{8c}$$

Thus, using equation (5), (6) and (7), one gets

$$\ln k = \ln\left(\frac{x_A^p x_B}{x_{ApB}}\right) + \frac{\omega_{12}}{RT}[px_B(1 - x_B) + x_A] + \frac{\omega_{13}}{RT}[px_{ApB}(1 - x_A) - x_A] + \frac{\omega_{23}}{RT}[x_{ApB}(1 - px_B) - x_B] \tag{9}$$

Once the expressions for G_M is obtained, other thermodynamic and microscopic functions follow readily. Heat of mixing, entropy of mixing and concentration fluctuations in the long-wavelength limit are related to G_M through standard thermodynamic relations

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{T,P} \tag{9}$$

$$S_M = \frac{H_M - G_M}{T} \tag{10}$$

$$S_{CC}(0) = RT(\partial^2 G_M / \partial C^2)_{T,P}^{-1} \tag{11a}$$

$$S_{CC}(0) = (1-C)a_1(\partial a_1 / \partial C)_{T,P}^{-1}$$
$$= Ca_2(\partial a_2 / \partial(1-C))_{T,P}^{-1} \tag{11b}$$

where C (= x_{Mg}) is concentration of A component in the alloy. Equation (7) is used in equation (9) and (11), we obtained expressions for H_M and $S_{CC}(0)$ as

$$H_M = \frac{1}{(1+px_{ApB})}(x_A x_B \omega_{12} + x_A x_{ApB}\omega_{13} + x_B x_{ApB}\omega_{23}) - \frac{T}{(1+px_{ApB})} \times$$

$$\left(x_A x_B \frac{\partial \omega_{12}}{\partial T} + x_A x_{ApB}\frac{\partial \omega_{13}}{\partial T} + x_B x_{ApB}\frac{\partial \omega_{23}}{\partial T}\right) - \frac{x_{ApB}}{(1+px_{ApB})}RT^2\frac{d\ln k}{dT}$$

(12)

$$S_{CC}(0) = \left\{\frac{1}{(1+px_{ApB})}\left[\frac{2}{RT}(x'_A x'_B \omega_{12} + x'_A x'_{ApB}\omega_{13} + x'_B x'_{ApB}\omega_{23}) + \left(\frac{x'^2_A}{x_A} + \frac{x'^2_B}{x_B} + \frac{x'^2_{ApB}}{x_{ApB}}\right)\right]\right\}^{-1} \tag{13}$$

Here, $\frac{\partial^2 \Delta G}{\partial C^2} > 0$ for $\frac{\partial \Delta G}{\partial C} = 0$

where prime denotes the differentiations with respect to concentration and x'_A and x'_B are determined by using equation (5). x'_{ApB} is determined using the equation (9) and the condition $\frac{d\ln k}{dC} = 0$ [3].

The concentration fluctuation in long wavelength limit ($S_{CC}(0)$) can be determined from measured activity data following equations (11b) [13]. This is usually considered as the experimental value.
In order to fit the degree of order in the liquid alloy, Warren- Cowley short-range parameter α_1 [14, 15] can be estimated from the knowledge of concentration-concentration structure factor S$_{CC}$(q) and the number-number structure factor S$_{NN}$(q). However, in most diffraction experiments these quantities are not easily measurable for all kinds of binary liquid alloy [16, 17]. On the other hand α_1 can be estimated from the knowledge of S$_{CC}$(0) [18,19]

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}, \qquad S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)}; \qquad S_{CC}^{id} = C(C-1) \tag{14}$$

where Z is coordination number and Z =5 is taken for our calculation. We note that varying the value of Z does not have any effect on the position of the minima of α_1; the effect is to vary the depth while the overall feature remains unchanged.

The pairwise interaction energies and equilibrium constant are determined by the following method:

In a regular associated solution $x_1\gamma_1 = x_A\gamma_A$ and $x_2\gamma_2 = x_B\gamma_B$, where γ_1 and γ_2 are respective gross activity coefficients of components 1 and 2. Thus

$$\ln\gamma_1 = \ln\gamma_A + \ln\frac{x_A}{x_1} \tag{15a}$$

and

$$\ln\gamma_2 = \ln\gamma_B + \ln\frac{x_B}{x_2} \tag{15b}$$

Following the technique of Lee and Ramchandrarao [1] the pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be written as

$$\ln\gamma_1^0 = \frac{\omega_{12}}{RT} \tag{16a}$$

$$k\exp(\omega_{13}/RT) = \frac{\gamma_1^o\gamma_2^o}{\gamma_1^o - \gamma_2^o} \tag{16b}$$

where γ_1^o and γ_2^o are activity coefficients of component A and that of B at zero concentrations. Solving equations (8a) and (8b) we obtain

$$\frac{\omega_{13}}{RT} = \frac{x_B\ln\left(\frac{a_2}{x_B}\right) + (1-x_B)\ln\left(\frac{a_1}{x_A}\right) - x_B(1-x_B)\frac{\omega_{12}}{RT}}{x_{ApB}^2} \tag{17}$$

$$\frac{\omega_{23}}{RT} = \frac{x_A\ln\left(\frac{a_1}{x_A}\right) + (1-x_A)\ln\left(\frac{a_2}{x_B}\right) - x_A(1-x_A)\frac{\omega_{12}}{RT}}{x_{ApB}^2} \tag{18}$$

where a_1 and a_2 are respective activities of Mg and Tl atoms in the liquid alloys.

Using equations (9), (17) and (18), we can derive

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{ApB}}\right)\ln\left(\frac{a_1}{x_A}\right) + \frac{x_B}{x_{ApB}}\left[\ln\left(\frac{a_2}{x_B}\right) - \frac{\omega_{12}}{RT}\right] + \ln\left(\frac{a_1^p a_2}{x_{ApB}}\right) \tag{19}$$

3. Results and Discussion

The mole fraction of complex $Mg-Tl$ is determined using experimental data of activity [9] and equations (16) and (19) employing the iterative procedure. The best fit values of equilibrium constant and pairwise interaction energies for the alloy Mg_2Tl in liquid state at 923 K are found to be

$$k = 0.113, \quad \omega_{12} = -20940 \text{ J mol}^{-1}, \quad \omega_{13} = -7870 \text{ J mol}^{-1} \text{ and } \quad \omega_{23} = -29050 \text{ J mol}^{-1}$$

All the interaction energies are negative and show that Mg and Tl atoms are attracted to each other and to the complex.

The compositional dependence of various species (Fig. 1) shows that the maximum association occurs at 60 at. pct. of Mg. At this composition and 923 K, about 21 mol pct. of the liquid alloy is associated.

Theoretical calculation of free energy of mixing for Mg-Tl liquid alloy shows that it is moderately interacting system. Fig. 2 shows excellent agreement between the experimental and calculated free energies. The free energy of mixing is minimum (= -12.6 kJ) at x_{Mg} = 0.5 which is almost equal to the experimental result [1]. Fig. 2 shows an excellent agreement between the experimental and calculated free energies.

On using equation (12) and observed values of H_M [1], we have chosen the following values for the given parameters as the best fit values for the heat of formation of Mg-Tl complex.

$$\frac{\partial \omega_{12}}{\partial T} = -10 \, \text{Jmol}^{-1}\text{K}^{-1}, \frac{\partial \omega_{13}}{\partial T} = +22.5 \, \text{Jmol}^{-1}\text{K}^{-1}, \quad \frac{\partial \omega_{23}}{\partial T} = +2 \, \text{Jmol}^{-1}\text{K}^{-1} \quad \text{and} \quad R \, T^2 \frac{\partial \ln k}{\partial T} =$$
$$14250 \pm 800 \, \text{J mol}^{-1}$$

It is found from the analysis that the heat of mixing is negative at all concentration. Our theoretical calculation shows that the minimum value of the heat of mixing is -6.87 kJ at x_{Mg} = 0.6. Further it is observed that the concentration dependence of asymmetry in H_M can be explained only when one considers the temperature dependence of the pairwise interaction energies. Theoretical values of heat of mixing are in very good agreement with observed values.
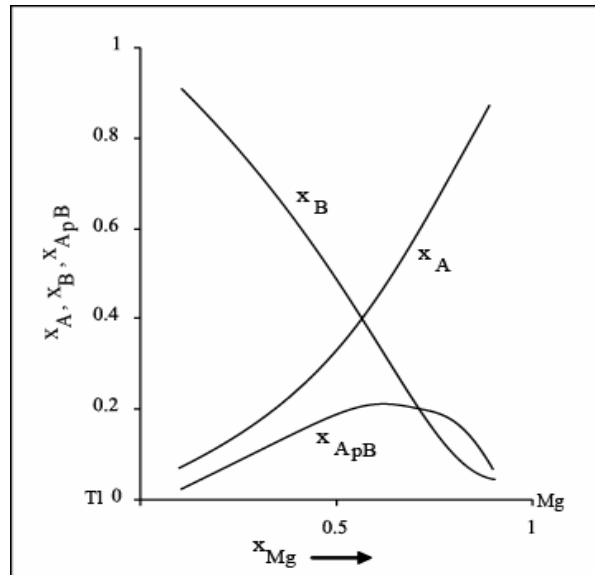

Fig.-1 : Compositional dependence of mole fractions x_A (A=Mg), x_B (B=Tl) and x_{ApB} (ApB= Mg$_2$Tl) versus x_{Mg} (concentration of Mg) at 923K.
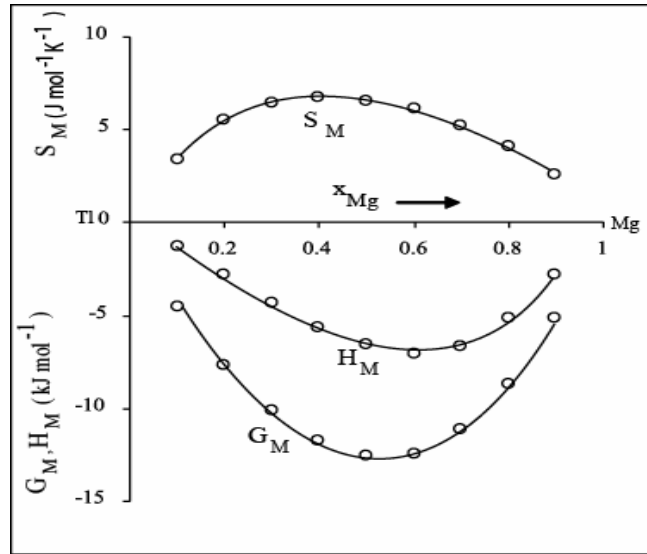
Fig.-2 : Upper part : Entropy of mixing (S_M) versus x_{Mg}, Lower part : free energy of mixing (G_M) and heat of mixing (H_M) versus x_{Mg} (concentration of Mg) at 923K; (——) theory, (ooo) experiment [1].

We have calculated entropy of mixing of Mg-Tl alloy in liquid state using equation (10). The calculated values always match in sign with observed values. The calculated values and experimental values are in good agreement in all concentration of Mg. The concentration dependence of asymmetry in S_M is well explained (Fig. 2).

The basic inputs for the calculations of activity are pairwise interaction energies and mole fractions of the unassociated atoms of component 1, called A, unassociated atoms of component 2, called B and the complex, ApB. We have used the same values of mole fractions and pairwise interaction energies for the evaluation of activity which were used for the evaluation of free energy of mixing, heat of mixing and entropy of mixing. The agreement between observed and calculated values of activity of Mg and Tl is also good as shown in Fig. 3.

Fig. 4 shows the computed and experimental values of Scc(0) as well as ideal values. The calculated values for Scc(0) shows excellent agreement with the experimental values. The Scc(0) can be used to understand the nature of atomic order in the binary liquid alloys. At a given composition, if Scc(0) < $S_{CC}^{id}(0)$, ordering in liquid alloy is expected and if Scc(0) > $S_{CC}^{id}(0)$, there is tendency of segregation. Our theoretical analysis clearly indicates that, there is unlike atoms are pairing as nearest neighbours in full range of concentration of Mg, i.e., Mg-Tl alloy in the liquid state behaves like unlike atoms ordering pair in whole concentration range.

The knowledge of α_1 provides an immediate insight into the nature of the local arrangements of atoms in the mixture. At equiatomic composition, one has $-1 \le \alpha_1 \le 1$. The minimum possible value of α_1 is $\alpha_1^{min} = -1$ and that implies complete ordering of unlike atoms paring at nearest neighbours. On the other hand the maximum value of α_1 is $\alpha_1^{max} = +1$ which implies total segregation leading to the phase separation and α_1 = 0 corresponds to a random distribution of atoms. The variation of α_1 (Fig. 4) clearly strengthens the result obtained from the study of $S_{CC}(0)$.
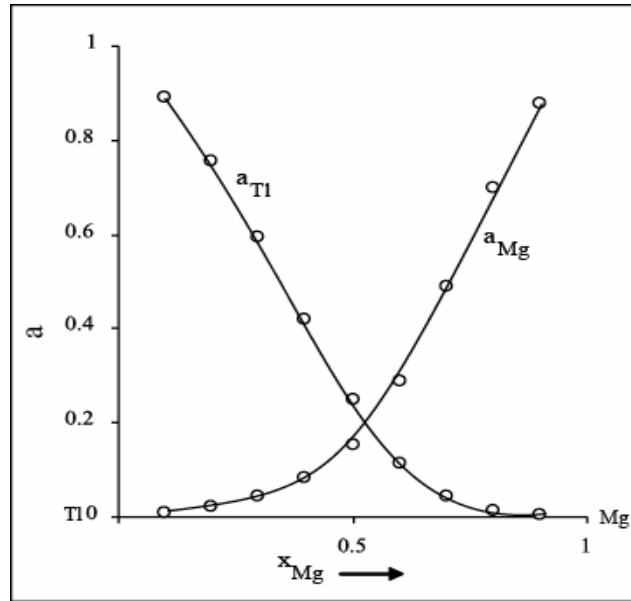
Fig.-3 : Activity (a) of Mg and Tl in liquid Mg-Tl liquid alloy at 923K versus x_{Mg} ; (——) theory, (∘∘∘) experiment [1].
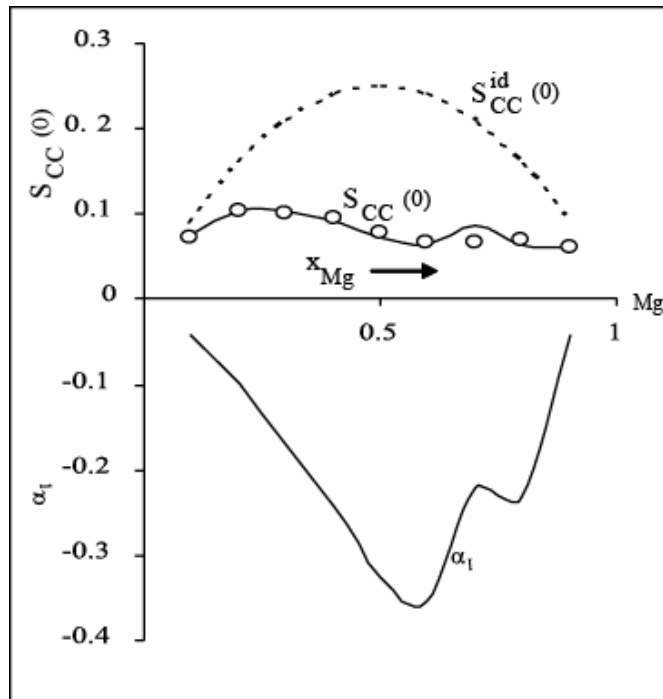

Fig.-4 : Upper part : Concentration fluctuations in long wavelength limit ($S_{cc}(0)$) versus x_{Mg} (concentration of Mg) at 923K ; Lower part : short range ordering parameter (α_1) versus x_{Mg} at 923K; (——) theory, (∘∘∘) experiment, (----) ideal values.

4. Conclusion

The thermodynamic properties and microscopic structure of Mg-Tl alloy in liquid state are explained assuming Mg_2Tl complex in the melt on the basis of regular associated solution model The analysis suggests that there is a tendency of unlike atom pairing (Mg-Tl) in Mg-Tl alloy whole range of concentration. The result also indicates that there exist Mg_2Tl complex in the liquid state of Mg-Tl alloy.

Acknowledgement

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