

Thermo-Physical Properties of Al-Mg Alloy in Liquid State at Different Temperatures

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Abstract

Thermo-physical properties of Al-Mg alloys in molten state at 1073 K have been studied using thermodynamic modeling. Thermodynamic properties, such as free energy of mixing, heat of mixing, entropy of mixing, activities and structural properties, such as concentration fluctuation in long wavelength limit, Warren-Cowley short range order parameter have been studied at 1073 K, 1173 K, 1273 K and 1373 K on the basis of regular associated solution model. The surface properties such as surface concentrations and surface tension of the liquid alloys have been studied by using Butler's model. A consistent set of model parameters have also been obtained by using optimization procedure based on statistical thermodynamics. Our analysis reveals that Al-Mg alloy is moderately interacting and it shows ordering nature at 1073 K. The nature of the alloys changes from ordering to segregating as the temperature increases.

Keywords

True Mole Fraction, Pairwise Interaction Energy, Temperature Derivative Terms, Al_3Mg_2 Complex, Optimization Procedure

1. Introduction

The properties such as light weight and excellent corrosion resistance make Al-based alloys suitable for developing engineering structures and their components. Because of these properties Al-based alloys have been extensively used in aircraft, automotive engines and architecture [1] [2] [3]. Apart from aforementioned properties, Al-Mg alloys have other very valuable properties, such as high

mechanical strength, good crack resistance, low cost maintenance, non-toxic, non-magnetic and much less inflammable than any other Al-based alloys. This is why a considerable attention has been given by metallurgist in developing Al-Mg alloys because of the possibilities of their uses in electrical industry, roofing sheets, vehicle paneling etc. [4] [5] [6] [7]. The Al-Mg alloys in liquid state had also been studied by theoreticians [8] [9] in the past. But these studies were only for a particular temperature; say 1073 K at which observed property is available. In present work, we have studied the thermodynamic, structural and transport properties of Al-Mg liquid alloys at different temperatures. These properties are then assessed by optimization procedure which is the thermodynamic description based on statistical thermodynamics or polynomial expressions.

There have been several studies based on the multiple theoretical models for the study of the mixing properties of liquid alloys [8]-[17]. In present work, we study the thermodynamic and structural properties of liquid Al-Mg alloys at different temperatures using regular associated solution model (RASM) [16] [17] [18] [19]. The surface tension of the alloy has been studied by Butler's model [20]. In previous works, we used RASM to study the properties of binary liquid alloys having complexes $A_\mu B_\nu$ with $\mu \geq 1$ and $\nu = 1$ [16] [17] [18] [19] [21] [22]. The phase diagram of Al-Mg alloys [23] indicates that there exists an Al_3Mg_2 complex in the mixture. So we also assume the existence of the same complex in Al-Mg liquid alloys near melting temperature. Here $\mu = 3$ and $\nu = 2$. Thus the input parameters are obtained by using the expressions different from previous ones, which will be explained in section 2 of this article.

In RASM, the existence of complexes in binary solution is assumed and hence a binary alloy in molten state can be treated as a ternary mixture of monomers and complexes; all in chemical equilibrium [8] [16] [17] [19]. However, the interactions between both the unassociated atoms and the complex are not necessarily equal and therefore unassociated atoms may not interact equally with the complex [18] [19] [21] [22] [24]. The advantage of the RASM is that the most of the input parameters are computed by solving mathematical expressions [17] [18] [19] [24] [25] where as in most of the models the input parameters are estimated just by fitting methods.

The paper is organized as follows: In Section 2, the theoretical framework is presented. Section 3 gives the results and discussion of the work. Finally, the conclusions are outlined in Section 4.

2. Formalism

2.1. Thermodynamic Properties

We consider a mixture of Al and Mg metals in molten state which on the basis of RASM [16] [17] [18] [19] leads to a pseudo-ternary mixture of Al-Al, Mg-Mg monomers and $Al_\mu Mg_\nu$ complexes at equilibrium, where $\mu = 3$ and $\nu = 2$ [23]. On the basis of previous works [17] [18] [21] [25], it can be assumed that the thermodynamic properties of the liquid mixture is overruled by their true mole frac-

tions $x_A (= x_{Al})$, $x_B (= x_{Mg})$ and $x_{Al-Mg} (= x_{A-B})$ in spite of their gross fractions $C_{Al} (= x_1)$ and $C_{Mg} (= 1 - x_1 = x_2)$. Relations between true mole fractions and gross mole fractions for Al-Mg ($= Al_\mu Mg_\nu$) alloys at molten state can be developed using regular associated solution model and is given as

$$x_A = x_1 [1 + (\mu + \nu - 1)x_{A-B}] - \mu x_{A-B} \quad (1)$$

$$x_B = x_2 [1 + (\mu + \nu - 1)x_{A-B}] - \nu x_{A-B} \quad (2)$$

On the basis of RASM, the expression of free energy of mixing, (G_M) can also be derived [16] [17] [18] [19] [24] [25] and is given as

$$G_M = \frac{1}{1 + (\mu + \nu - 1)x_{A-B}} \left[(x_A x_B \omega_{12} + x_A x_{A-B} \omega_{13} + x_B x_{A-B} \omega_{23}) + RT (x_A \ln x_A + x_B \ln x_B + x_{A-B} \ln x_{A-B}) + x_{A-B} RT \ln k \right] \quad (3)$$

where ω_{12} , ω_{13} , ω_{23} are respective interaction energy parameters between the pairs A, B; A, A-B and B, A-B respectively. R is Universal gas constant, T the temperature and k the equilibrium constant to be estimated.

The equilibrium constant, k , is given as [16] [17] [25]

$$k = \frac{x_A^\mu x_B^\nu \gamma_A^\mu \gamma_B^\nu}{x_{A-B} \gamma_{A-B}} \quad (4)$$

The activity coefficients γ_A for monomer A, γ_B for monomer B and γ_{A-B} for the complex A-B can be expressed in terms of true mole fractions and interaction energy parameters as [17] [24] [25]

$$RT \ln \gamma_A = x_B^2 \omega_{12} + x_{A-B}^2 \omega_{13} + x_B x_{A-B} (\omega_{12} - \omega_{23} + \omega_{13}) \quad (5a)$$

$$RT \ln \gamma_B = x_{A-B}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{A-B} (\omega_{23} - \omega_{13} + \omega_{12}) \quad (5b)$$

$$RT \ln \gamma_{A-B} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_A x_B (\omega_{13} - \omega_{12} + \omega_{23}) \quad (5c)$$

The activity coefficients for pure components and monomers are connected by the relations [17] [26]

$$x_1 \gamma_1 = x_A \gamma_A \quad \text{and} \quad x_2 \gamma_2 = x_B \gamma_B \quad (6)$$

where γ_1 and γ_2 are gross activity coefficients of pure components A and B respectively.

The activity coefficients of monomers at infinite dilution can be related to the pairwise interaction energies by the following expressions [17]

$$\ln \gamma_1^0 = \frac{\omega_{12}}{RT} \quad (7)$$

$$k \exp(\omega_{13}/RT) = \frac{\gamma_1^0 \gamma_2^0}{\gamma_1^0 - \gamma_2^0} \quad (8)$$

where γ_1^0 and γ_2^0 are respective activity coefficients at zero dilutions.

On solving Equations (5a) and (5b) for $\frac{\omega_{13}}{RT}$ by substituting $x_A + x_B + x_{A-B} = 1$, yields

$$\frac{\omega_{13}}{RT} = \frac{x_B \ln \left(\frac{a_2}{x_B} \right) + (1 - x_B) \ln \left(\frac{a_1}{x_A} \right) + x_B (1 - x_B) \frac{\omega_{12}}{RT}}{x_{A-B}^2} \quad (9a)$$

Similarly, the expression for $\frac{\omega_{23}}{RT}$ can be obtained by solving Equations (5a) and (5b) as

$$\frac{\omega_{23}}{RT} = \frac{x_A \ln\left(\frac{a_1}{x_A}\right) + (1-x_A) \ln\left(\frac{a_2}{x_B}\right) + x_A(1-x_A) \frac{\omega_{12}}{RT}}{x_{A-B}^2} \quad (9b)$$

where a_1 and a_2 are activities of the pure components A and B respectively.

The expression for the mole fraction of the complex in terms of interaction energies and activity of pure components of the alloy can be obtained by using Equation (9) in Equations (4) and (5) along with algebraic simplification as follows [17]

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{A-B}}\right) \ln\left(\frac{a_1}{x_A}\right) + \left(\frac{x_B}{x_{A-B}}\right) \left[\ln\left(\frac{a_2}{x_B}\right) - \frac{\omega_{12}}{RT} \right] + \ln\left(\frac{a_1^\mu a_2^\nu}{x_{A-B}}\right) \quad (10)$$

The heat of mixing, H_M in terms of G_M is given by

$$H_M = G_M - T \left(\frac{\partial G_M}{\partial T} \right)_P \quad (11)$$

Using Equations (3) and (11) we get

$$H_M = \frac{1}{1+(\mu+\nu-1)x_{A-B}} \left[(x_A x_B \omega_{12} + x_A x_{A-B} \omega_{13} + x_B x_{A-B} \omega_{23}) - T \left(x_A x_B \frac{\partial \omega_{12}}{\partial T} + x_A x_{A-B} \frac{\partial \omega_{13}}{\partial T} + x_B x_{A-B} \frac{\partial \omega_{23}}{\partial T} \right) + x_{A-B} RT^2 \frac{d \ln k}{dT} \right] \quad (12)$$

where $\frac{\partial \omega_{12}}{\partial T}$, $\frac{\partial \omega_{13}}{\partial T}$ and $\frac{\partial \omega_{23}}{\partial T}$ are temperature derivatives of interaction energy parameters.

The entropy of mixing, S_M can be obtained by using standard thermodynamic relations

$$S_M = \frac{H_M - G_M}{T} \quad (13)$$

2.2. Structural Properties

The structural properties of the molten alloys can be assessed by means of concentration fluctuation in long wavelength limit ($S_{CC}(0)$). The relation of $S_{CC}(0)$ with G_M given as [10]

$$S_{CC}(0) = RT \left(\frac{\partial^2 G_M}{\partial^2 x_1} \right)_{T,P}^{-1} \quad (14)$$

Using Equation (3) in Equation (14) implying the constrains $\frac{\partial G_M}{\partial x_1} = 0$ for

$$\left(\frac{\partial^2 G_M}{\partial^2 x_1} \right) > 0 \quad \text{and} \quad \frac{d \ln k}{dx_1} = 0 \quad [18] \quad \text{yields}$$

$$S_{CC}(0) = \left\{ \frac{1}{1 + (\mu + \nu - 1)x_{A-B}} \left[\frac{2}{RT} (x'_A x'_B \omega_{12} + x'_A x'_{A-B} \omega_{13} + x'_B x'_{A-B} \omega_{23}) + \left(\frac{x'^2_A}{x_A} + \frac{x'^2_B}{x_B} + \frac{x'^2_{A-B}}{x_{A-B}} \right) \right] \right\}^{-1} \quad (15)$$

where primes in true mole fractions denote the differentiations with concentrations. The observed value of the $S_{CC}(0)$ is obtained by the relations [10].

$$S_{CC}(0) = (1 - x_1) a_1 \left(\frac{\partial a_1}{\partial x_1} \right)_{T,P}^{-1} = x_1 a_2 \left(\frac{\partial a_2}{\partial (1 - x_1)} \right)_{T,P}^{-1} \quad (16)$$

To measure the degree of ordering of binary alloys in liquid states, the knowledge of the Warren-Cowley [27] [28] short range order parameter (α_1) is essential. The α_1 can be related to the $S_{CC}(0)$ by the relations [10] [11]

$$\alpha_1 = \frac{S - 1}{S(Z) + 1}, \text{ with } S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)} \quad (17)$$

where, Z is the coordination number of the alloy and it is taken as 10 for our calculation. The value of Z does not vary the nature of α_1 ; the effect is to vary the depth not the overall features.

2.3. Surface Properties

If the bulk and hypothetical surface of a solution is assumed to be in equilibrium (Butler's approach [20]) the surface tension of a liquid solution can be expressed as [20] [29]

$$\sigma = \frac{\mu_1^s - \mu_1^b}{\alpha_1} = \frac{\mu_2^s - \mu_2^b}{\alpha_2} = \dots = \frac{\mu_i^s - \mu_i^b}{\alpha_i} \quad (18)$$

where σ , μ_i^s , μ_i^b and α_i are surface tension of the solution, chemical potential in the bulk and that in the hypothetical surface and molar surface area of i th component respectively. The chemical potential in the surface and in the bulk are related to the respective compositions and can be expressed by the same equation in the surface and in the bulk as follows [29]

$$\mu_i^s = \mu_i^{s0} + RT \ln x_i^s, \quad \mu_i^b = \mu_i^{b0} + RT \ln x_i^b \quad (19)$$

where x_i^s and x_i^b are the mole fraction of i th component of the solution in the surface and that in the bulk respectively. For real solution the mole fraction is replaced by the activities because the activity coefficient is different from unity. Replacing the mole fractions by corresponding activities in Equation (19) and rearranging the equation, we get [20] [30]

$$\sigma = \sigma_1 + \frac{1}{\alpha_1} (G_1^{E,s} - G_1^{E,b}) + \frac{RT}{\alpha_1} \ln \left(\frac{x_1^s}{x_1^b} \right) = \sigma_2 + \frac{1}{\alpha_2} (G_2^{E,s} - G_2^{E,b}) + \frac{RT}{\alpha_2} \ln \left(\frac{x_2^s}{x_2^b} \right) \quad (20)$$

where $G_i^{E,s}$ and $G_i^{E,b}$ are the partial excess free energy of mixing in the surface and that in the bulk. It may be proper to mention that $x_1^s + x_2^s = 1$ and $x_1^b + x_2^b = 1$.

The molar surface area of a pure component i in the liquid state can be expressed as [30]

$$\alpha_i = f (V_i^0)^{2/3} (N)^{1/3} \quad (21)$$

where N is Avogadro's constant, V_i^0 is the molar volume of the pure component i at its melting temperature and f is the geometrical constant. The geometrical constant can be expressed as

$$f = \left(\frac{3f_b}{4} \right)^{2/3} \frac{\pi^{1/3}}{f_s} \quad (22)$$

where f_b is the volume packing fraction and f_s is the surface packing fraction. Their values depend upon the type of crystal structure of the pure components of the alloys.

2.4. Optimization Procedure Thermodynamic, Structural and Surface Properties

A consistent set of model parameters in an analytical approach can be obtained by the optimization procedure which is the thermodynamic description based on statistical thermodynamics or polynomial expressions. The adjustable coefficients, used in the process, are estimated by least square method which gives an idea to extrapolate into temperature and concentration region in which the direct observed determination is unavailable.

The various thermodynamic properties, described by a power-series law whose coefficient are A, B, C, D, E, \dots (say), are determined by least-square method [31]. The heat capacity can be expressed as

$$C_p = -C - 2DT - 2ET^{-2} \quad (23)$$

From the thermodynamic relation, the heat of mixing and entropy of mixing are given by

$$H = H(T_0) + \int_0^T C_p dT = A - CT - DT^2 + 2ET^{-1} - \dots \quad (24)$$

$$S = S(T_0) + \int_0^T \frac{C_p}{T} dT = -B - C(1 + \ln T) - 2DT + ET^{-2} - \dots \quad (25)$$

Using Equations (24) and (25) in the thermodynamic relation, $G_M = H - TS$, we get the temperature (T) dependent free energy as

$$G = A + BT + CT \ln T + DT^2 + ET^{-1} + \dots \quad (26)$$

Redlich-Kister polynomial equation gives the composition dependence of excess free energy of mixing and is given by

$$G_M^{XS}(c, T) = c(1-c) \sum_{i=0}^m K_i(T) [c - (1-c)]^i \quad (27)$$

with

$$K_i(T) = A_i + B_i T + C_i T \ln T + D_i T^2 + \dots \quad (28)$$

The coefficients K_i is the function of the temperature same as that of G in Eq-

uation (26). The least-square method can be used to obtain the parameters involved in Equation (26). For this purpose, we calculate the excess free energy of mixing (G_M^{XS}) of the Al-Mg liquid alloy at different temperatures by the relation

$$G_M^{XS} = G_M - G_M^{id} \quad (29)$$

3. Results and Discussion

3.1. Thermodynamic, Structural and Surface Properties at 1073 K

3.1.1. Thermodynamic Properties

The input parameter $\frac{\omega_{12}}{RT}$ was computed from the Equation (7) using activity coefficient of Al at zero dilution. The mole fractions of the complex $x_{\text{Al-Mg}}$ and the unassociated components $x_{\text{Al}}, x_{\text{Mg}}$ were estimated by using Equations (7) and (8) in (10) with the knowledge of observed activities [23] of pure components of Al-Mg alloy in liquid state at 1073 K. The compositional dependence of mole fractions (Figure 1) shows that the maximum association between the components of the alloy occurs at $C_{\text{Al}} = 0.6$ which is compound forming concentration ($= \frac{\mu}{\nu + \nu} = \frac{3}{2+3} = 0.6$). At this concentration, about 16.1% of the alloy is associated. The other model parameters $\frac{\omega_{13}}{RT}$ and $\frac{\omega_{23}}{RT}$ were estimated by using Equations (9a) and (9b). These estimated values were slightly adjusted to explain the observed values of free energy of mixing at all concentrations [23]. The pairwise interaction energy parameters and equilibrium constant for Al-Mg alloys in liquid state at 1073 K were found as

$$\begin{aligned} \omega_{12} &= -6253.57 \text{ J} \cdot \text{mol}^{-1}, \omega_{13} = +30687.97 \text{ J} \cdot \text{mol}^{-1}, \\ \omega_{23} &= +16682.18 \text{ J} \cdot \text{mol}^{-1} \text{ and } k = 0.055 \end{aligned}$$

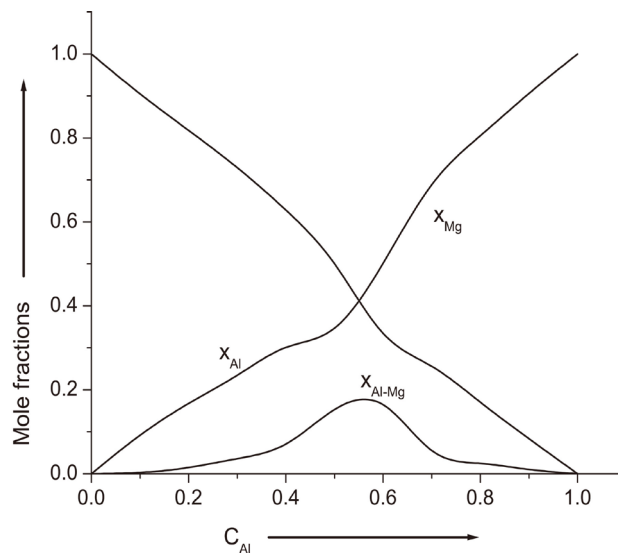


Figure 1. Compositional dependence of mole fractions of Al-Mg alloy in liquid state at 1073 K.

The negative value of ω_{12} shows that Al and Mg atoms in the liquid alloy are attracted to each other. Similarly, the positive value of ω_{13} and ω_{23} show that there is repulsion between Al atoms and the complexes Al-Mg and Mg atoms and the complexes Al-Mg respectively.

The free energy of mixing was computed from Equation (3) by using aforementioned model parameters. There is good agreement between the computed and observed value of free energy of mixing (Figure 2). It has been observed that both the computed and observed values of free energy of mixing are minimum at equiatomic composition ($C_{Al} = 0.5$). Moreover, the computed values of excess free energy of mixing at equiatomic composition and temperature ($= -0.2778RT$) indicates that the system is moderately interacting and hence the affinity towards the compound formation is moderate.

On using Equation (12) and observed heat of mixing [23] the optimized value of the following parameters were found as

$$\begin{aligned}\frac{\partial\omega_{12}}{\partial T} &= +5.44 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \frac{\partial\omega_{13}}{\partial T} = +23.00 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \\ \frac{\partial\omega_{23}}{\partial T} &= +9.67 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{ and } RT^2 \frac{d \ln k}{dT} = 30000 \pm 1850 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

The need of aforementioned temperature derivative terms of interaction energy parameters to explain the observed heat of mixing clearly indicates that the pairwise interaction energy parameters are strongly dependent on temperature. There is good agreement between the computed and observed values of heat of mixing at all concentration except at or about equiatomic composition (Figure 3). Both the computed and observed values of heat of mixing are minimum at $C_{Al} = 0.54$. At this composition, the computed value of $\frac{H_M}{RT}$ is $-0.4053RT$ where as the corresponding observed values is $-0.3814RT$ [23]. This low negative value suggests that the bonding between the species Al and Mg to form the complex is weak. The entropy of mixing for the alloys was also computed using Equation (13). Both the computed and observed values of entropy of mixing were found to be in good agreement (Figure 3).

The activities of the components of the alloys were computed from Equations (5) and (6) using the same input parameters which were used for the computation of free energy of mixing, heat of mixing and entropy of mixing. The computed and observed values [23] were found to be in good agreement (Figure 4). The parameter, activity assesses the deviation of the system from the ideal behavior. Thus the knowledge of activities within a class of identical structure can be expected to offer, at least, a basis for correlation of the behaviour, which can then be used for extrapolation of the behaviour of a more complex system.

3.1.2. Structural Properties

The $S_{CC}(0)$ can be used to study the structural properties of the alloy at microscopic level [10]. The mixing and phase separation behavior in the binary liquid alloys can be predicted with the knowledge of the $S_{CC}(0)$. In general for

a liquid binary alloy, when the computed $S_{CC}(0)$ is greater than the ideal value, *i.e.* $S_{CC}(0) > S_{CC}^{id}$, there is homo-coordination or like atoms pairing in the alloy [10]. When $S_{CC}(0) < S_{CC}^{id}$, there is hetero-coordination or unlike atoms pairing and when $S_{CC}(0) = S_{CC}^{id}$, there is an ideal mixing of components [10]. The $S_{CC}(0)$ was computed by using Equations (15) and (16). Both the computed and the observed values of the $S_{CC}(0)$ are greater than the ideal values at all concentrations (Figure 5). This indicates that Al-Mg alloys in liquid state at 1073 K is ordering in nature at whole compositions.

The structural behaviour of the molten alloy can further be understood in terms of the Warren-Cowley short-range order parameter (α_1). The relative strength of the local order of atoms in the molten alloy is expressed in terms of

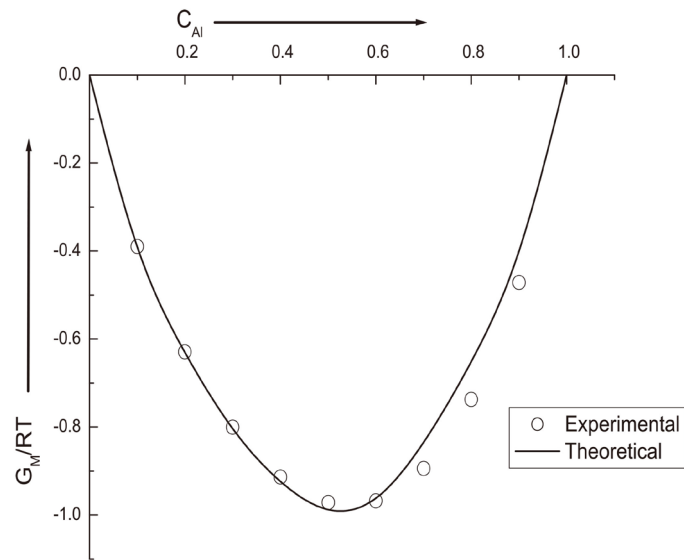


Figure 2. Compositional dependence of $(G_M/RT)_{Exp}$ and $(G_M/RT)_{Th}$ of Al-Mg liquid alloy at 1073 K.

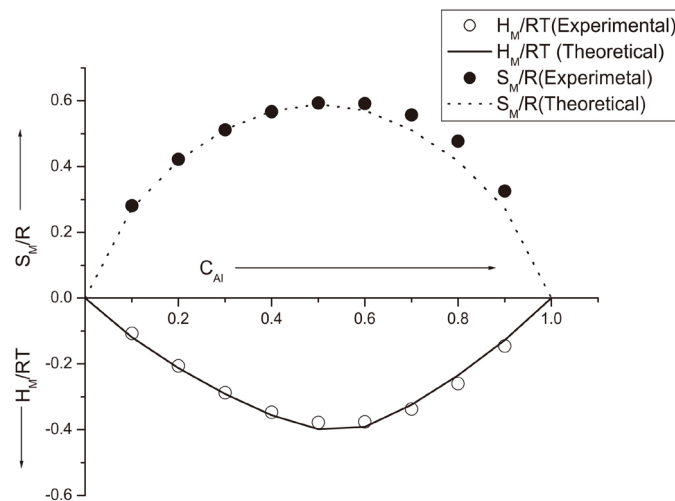


Figure 3. Compositional dependence of $(H_M/RT)_{Exp}$, $(H_M/RT)_{Th}$ and $(S_M/R)_{Exp}$, $(S_M/R)_{Th}$ of Al-Mg liquid alloy at 1073 K.

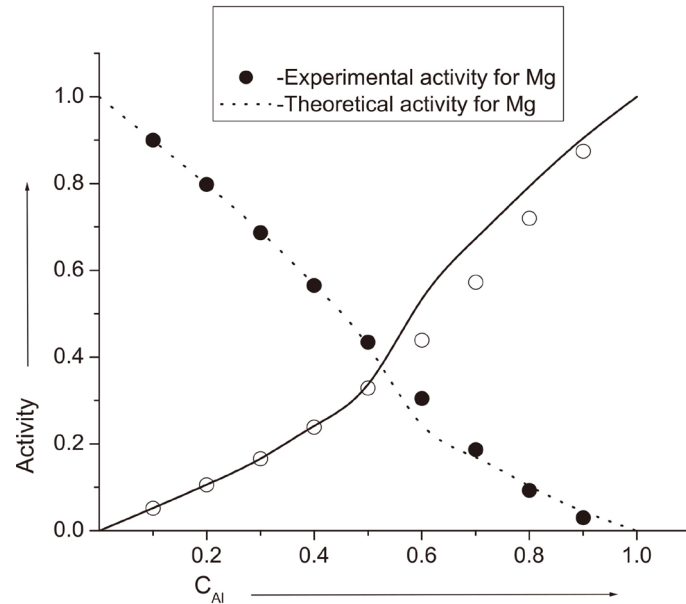


Figure 4. Compositional dependence of activity of Al-Mg liquid alloy at 1073 K.

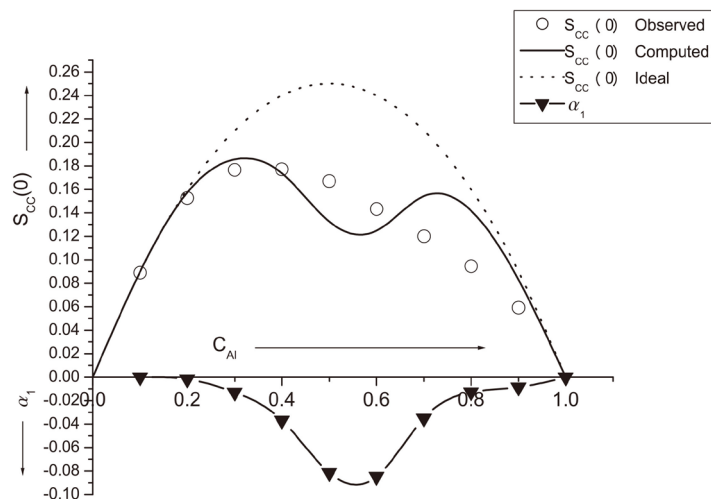


Figure 5. Compositional dependence of $(S_{cc}(0))_{\text{observed}}$, $(S_{cc}(0))_{\text{computed}}$, $(S_{cc}(0))_{\text{ideal}}$ and α_1 of Al-Mg liquid alloy at 1073 K.

normalized values of this parameter. The normalized value of the α_1 lies between -1 and $+1$. The positive values of α_1 indicate the phase separation (segregating); whereas the negative values of α_1 indicate the ordering (compound forming) in the binary liquid alloys. The value of α_1 is computed from Equation (17) and plotted in **Figure 5**. The α_1 was found negative at all compositions which indicates that Al-Mg alloys in liquid state at 1073 K is compound forming alloys in all compositions.

3.1.3. Surface Properties

The surface tension of the alloys in liquid state at 1073 K was calculated by using

Equation (20). For this, the properties, such as densities, surface tensions and partial excess free energies of the component metals at temperature of investigation are required. Densities ($\rho_i(T)$) and surface tensions ($\sigma_i(T)$) of the components Al and Mg metals at 1073 K were calculated from their values at respective melting temperatures using the following relations [32]

$$\begin{aligned}\rho_{\text{Al}}(T) &= 2345 - 0.2800 \times (T - T_{\text{Al},0}), \\ \rho_{\text{Mg}}(T) &= 1590 - 0.2647 \times (T - T_{\text{Mg},0}) \text{ (kg} \cdot \text{m}^{-3}\text{)}, \\ \sigma_{\text{Al}}(T) &= 0.914 - 0.35 \times 10^{-3} (T - T_{\text{Al},0}), \\ \sigma_{\text{Mg}}(T) &= 0.559 - 0.35 \times 10^{-3} (T - T_{\text{Mg},0}) \text{ (N} \cdot \text{m}^{-1}\text{)}\end{aligned}$$

where $T_{\text{Al},0} = 933 \text{ K}$, $T_{\text{Mg},0} = 924 \text{ K}$ and $T = 1073 \text{ K}$.

The bulk partial excess free energy of mixing for the individual components of the alloys in liquid state at 1073 K is available in [23]. We considered the geometrical constant $f = 1.061$ [30] and $\beta = \frac{G_i^{E,S}}{G_i^{E,B}} = 0.8181$ [30]. The computed values of surface concentrations for the components and surface tension of the solution were computed and plotted in **Figure 6** and **Figure 7** respectively. The surface concentration of Al is less than ideal values whereas that of Mg atoms is greater than ideal values at all compositions indicating that the former atoms remains in the bulk whereas later segregate on the surface of the solution at melting temperature. **Figure 7** shows that the surface tension of the solution is found to be less than ideal value in the entire range of concentrations at 1073 K.

3.2. Thermodynamic, Structural and Surface Properties at $T \geq 1073 \text{ K}$

In order to calculate the thermodynamic, structural and surface properties of alloys in liquid state at different temperatures we have made the following assumptions:

- 1) True mole fractions of the monomers and that of complex are temperature independent.
- 2) The pairwise interaction energies are temperature dependent.
- 3) The temperature dependence of pairwise interaction energies is linear above melting temperature.

Under these assumptions, the variation of interaction energy parameters with temperature can be expressed as

$$d[\omega_{ij}(T)]_C = \frac{\partial \omega_{ij}(T)}{\partial T} dT \quad (30)$$

where $i, j = 1, 2, 3$; $i \neq j$. C is the mole fraction.

$$\omega_{ij}(T_k) = \omega_{ij}(T) + \frac{\partial \omega_{ij}(T)}{\partial T} dT \quad (31)$$

where, $dT = T_k - T$; $T_k = 1173 \text{ K}, 1273 \text{ K}, 1373 \text{ K}$.

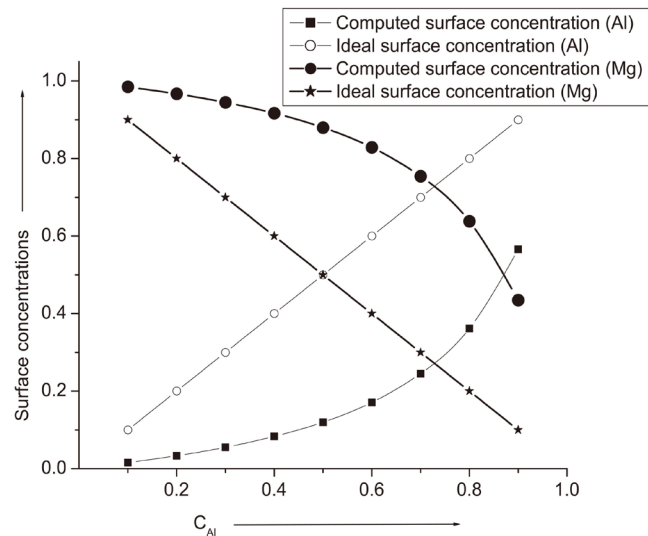


Figure 6. Compositional dependence of computed values of surface concentrations for the components of Al-Mg liquid alloy at 1073 K.

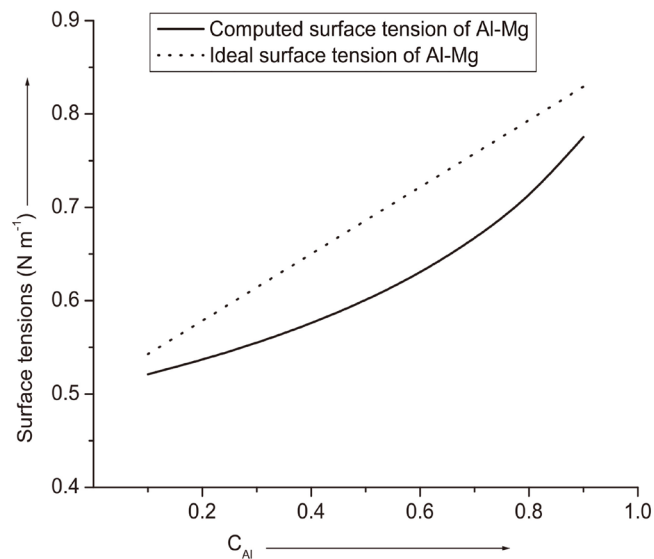


Figure 7. Compositional dependence of computed values of surface tension of Al-Mg liquid alloy at 1073 K.

Now the values of pairwise interaction energy parameters at 1073 K and their temperature derivatives were used in Equation (31) to obtain the pairwise interaction energy parameters at temperatures 1173 K, 1273 K and 1373 K. These input parameters were used in Equation (3) to estimate the free energy of mixing of the alloys at different temperatures. The computed values of free energy of mixing were then used to compute corresponding excess free energy of mixing using Equation (29). The model parameters for the prediction of thermodynamic properties of the alloys at any temperature were computed using Equations (27) and (28) optimization procedure (**Table 1**). The optimized values of free energy of mixing for Al-Mg alloys at different temperatures are plotted in **Figure**

8. The plot clearly shows that the free energy of mixing becomes smaller in magnitudes as the temperature increases. Thus the ordering behavior of the alloys will be weaker and weaker as the temperature increases.

The optimized value of partial excess free energy of mixing of the constituent X (\equiv Al) and Y (\equiv Mg) in Al-Mg liquid alloys are respectively given by

$$\tilde{G}_{M,X}^{XS}(c,T) = (1-c)^2 \sum_{l=0}^m K_l(T) [2c(l+1)-1] (2c-1)^{l-1} \quad (32)$$

and

$$\tilde{G}_{M,Y}^{XS}(c,T) = c^2 \sum_{l=0}^m K_l(T) [2c(l+1)-2l-1] (2c-1)^{l-1} \quad (33)$$

The activity coefficients of the components of the alloys at different temperatures were computed by the relations

$$\tilde{G}_{M,i}^{XS}(c,T) = RT \ln \gamma_i \quad (34)$$

where $i = \text{Al, Mg}$.

The activities of the components of the alloys at different temperatures were then computed by using the calculated values of the corresponding activity coefficients and plotted in **Figure 9**.

We computed the $S_{CC}(0)$ at different temperatures and plotted in **Figure 10**. The $S_{CC}(0)$ shifts towards the ideal values as the temperature increases. For concentrations $C_{\text{Al}} = 0.1-0.2$, the $S_{CC}(0)$ crosses the ideal values at $T \geq 1173$ K. This is a usual variation of the $S_{CC}(0)$ with temperature.

The values of the partial excess free energy of mixing computed from Equations (32) and (33) at required temperatures are fortune input parameters to calculate the surface tension of the liquid alloy at higher temperatures. The surface tension and hence the surface concentration of Al and Mg atoms of the system at temperatures 1173, 1273 and 1373 K are obtained from Equation (20) following the similar procedure as that for temperature 1073 K. The compositional and temperature dependence of the surface tension of the liquid Al-Mg alloy at higher temperatures is shown (**Figure 11**). It can be observed that the surface tension of the liquid alloy decreases with the increase in its temperature. The surface concentration of Al of the liquid alloy increases with increase in its temperature (**Figure 12**). The surface concentrations of Mg atoms of the liquid alloy decreases with the increase in its temperature. This indicates that the atoms in the bulk tend to segregate and the atoms in the surface tend to move to the bulk as the temperature increases.

Table 1. Calculated values of optimized coefficients A_l , B_l , C_l and D_l ($l = 0$ to 3) in liquid alloy Al-Mg.

l	A_l ($\text{J} \cdot \text{mol}^{-1}$)	B_l ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	C_l ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	D_l ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$)
0	-9.551×10^5	1.067×10^4	-1.494×10^3	0.590063
1	-2.620×10^6	2.988×10^4	-4.189×10^3	1.670447
2	-2.357×10^6	2.740×10^4	-3.852×10^3	1.567968
3	-7.793×10^5	9.349×10^3	-1.320×10^3	0.555166

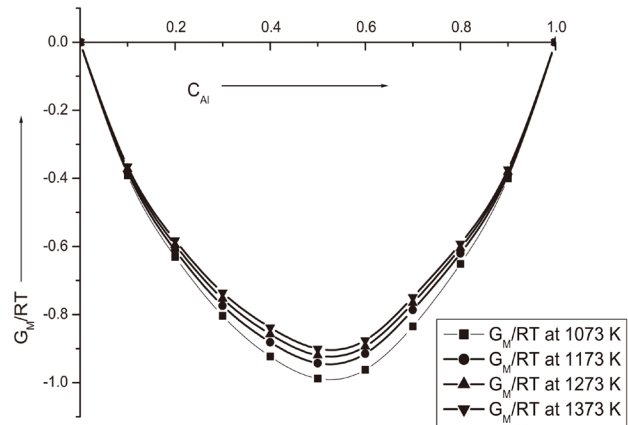


Figure 8. Compositional dependence of G_M/RT of Al-Mg liquid alloy at different temperatures.

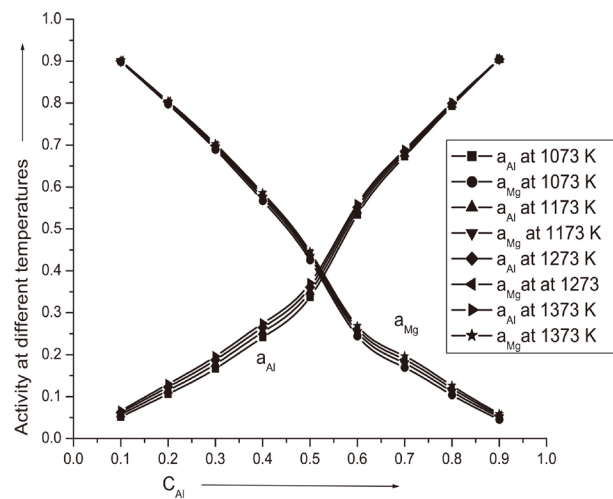


Figure 9. Compositional dependence of activity of Al-Mg liquid alloy at different temperatures.

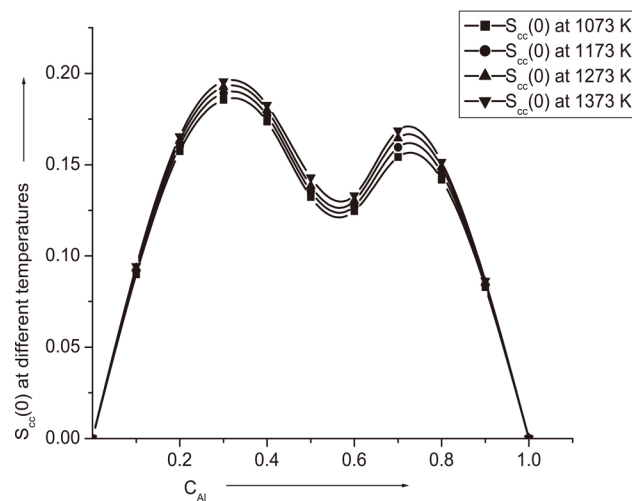


Figure 10. Compositional dependence $S_{cc}(0)$ of Al-Mg liquid alloy at different temperatures.

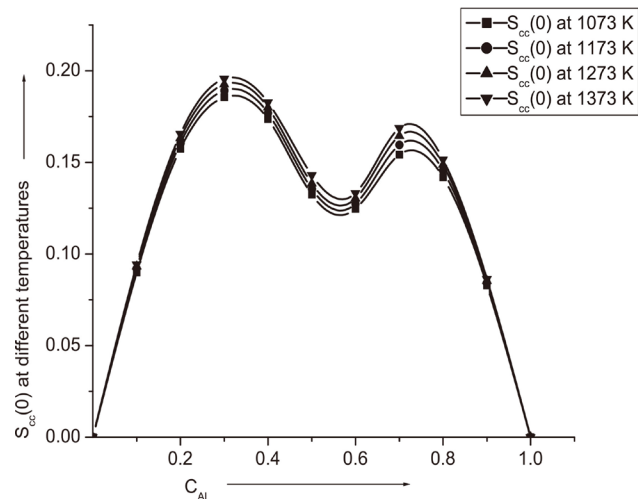


Figure 11. Compositional dependence of surface tensions of Al-Mg liquid alloy at different temperatures.

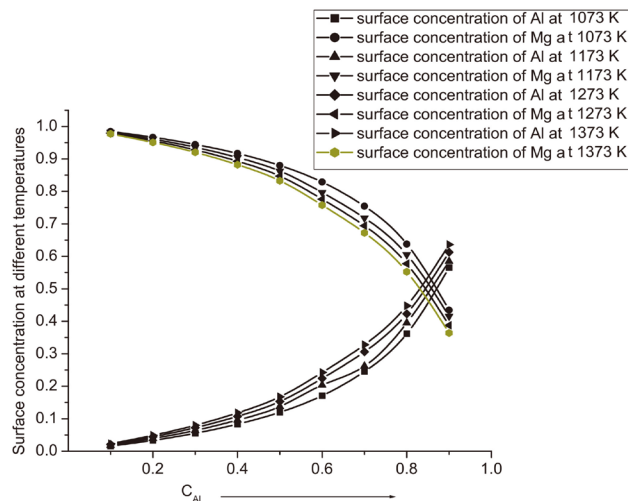


Figure 12. Compositional dependence of surface concentration of Al-Mg liquid alloy at different temperatures.

4. Conclusions

From our study the following conclusions can be drawn:

- 1) The Al-Mg liquid alloy is moderately interaction in nature.
- 2) The Al-Mg liquid alloy is ordering alloy at 1073 K. Above this temperature the nature of the alloy shifts towards the ideal nature.
- 3) Al atoms remain in the bulk and Mg atoms segregate in the surface.
- 4) The surface tension of the alloy is lesser than ideal values at all temperatures.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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