Theoretical assessment for the mixing properties of AlMg liquid alloys at 1073K

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Abstract. The alloying behavior of AlMg alloy in the liquid form at 1073 K has been theoretically investigated in the framework of four-parameter model which is based on Maclaurin series. The analytical expressions for thermodynamic functions such as excess free mixing energy, free mixing energy, enthalpy of mixing and entropy of mixing and microscopic functions such as concentration fluctuations at the long wavelength limit and Warren-Cowley chemical short range order parameter have been derived. These expressions have been used to compute the excess Gibbs free energy of mixing, Gibbs free energy of mixing, activity, enthalpy(heat) of mixing, excess entropy of mixing, entropy of mixing, concentration fluctuations in long wavelength limit and Warren-Cowley short range order parameters of AlMg liquid alloys at 1073 K. The investigation shows the excellent concurrence between the experimental and theoretical measurements of the mixing properties of AlMg liquid alloys at 1073 K. Interaction parameters of energy depends on temperature.

1. Introduction

Nowadays Al-based alloys are widely used in aircraft, automotive engines, engineering structures and components, electrical industries due to the properties like highly resist corrosion, lightweight structure and lower cost maintenance. Among Al-based alloys, AlMg alloys are most suitable for the replacement of steel from shipbuilding because they possess high mechanical strength, great resistance to corrosion, good ductility, durability, unfailed processing processes, and assuring lower cost production than the other Al-alloys [1-3]. Thus in the past AlMg liquid alloys have been found to be more attractive for the researchers [4-11].

The phase diagram [12] indicates that there are considerable number of binary alloys which exhibit asymmetries in the properties of mixing around the equiatomic composition, C= 0.5 due to the existence of chemical complexes in the solid state at one or more stoichiometric composition. The mixing properties of these alloys can’t be well explained on the basis of the size ratio and electro-negativities of the constituent atoms of the alloys. The size ratio and electro-negativities of the component atoms of these alloys cannot adequately explain the mixing properties of these alloys. Presuming the compound (or compound) may also exist in a liquid state explains the aspects of compound (or complex) properties of forming liquid alloys [13]. Thus, assuming the existence of chemical complexes in the liquid state of the alloys near the melting point, the compound (or complex) formation model [14-21] has been used to explain the thermodynamics properties of liquid alloys. The proposed investigation uses the four-parameter model [22-24] to explain the properties of the compound forming the AlMg liquid alloys at 1073 K without taking into account complex
formation. The four-parameter model has earlier been used to compute the thermodynamic properties like excess free energy of mixing, activity coefficients, activity and enthalpy of mixing of binary liquid alloys [22-24]. In present investigation, microscopic properties like concentration fluctuations in the long wavelength limit and short range order parameter have also been computed by four-parameter model to explain the nature of interaction among the constituent species of the binary alloy.

The phase diagram [12] shows the existence of Al$_3$Mg$_2$, Al$_{12}$Mg$_{17}$ and Al$_{30}$Mg$_{23}$ complexes in solid state. The excess free energy of mixing, $G^{XS}_M$ and the excess entropy of mixing $S^{XS}_M$ of AlMg liquid alloys at 1073 K are asymmetric about the equiatomic composition, $C=0.5$. $G^{XS}_M$ is minimum (i.e. $G^{XS}_M =-0.2956$) at $C_{Al}=0.6$ while $S^{XS}_M$ is minimum (i.e. $S^{XS}_M =-0.1057$) at $C_{Al}=0.4$ and $S^{XS}_M$ is positive at $C_{Al} = 0.9$. But the free energy of mixing, $G_M$ and the heat mixing, $H_M$ exhibit minima at the equiatomic composition, $C =0.5$. It is interesting to note that the entropy of mixing, $S_M$ of AlMg liquid alloys at 1073 K is positive throughout the range of concentration with maximum value at $C=0.5$. Therefore AlMg liquid alloy exhibits anomalous behavior, so comprehensive theoretical analysis is required. Thus for the understanding of the observed asymmetries as well as symmetries in the properties of mixing of compound forming AlMg liquid alloys at 1073 K, the four-parameter model has been applied without assuming the existence of chemical complexes in the alloys. The expressions for the various thermodynamic and microscopic functions have been derived in the framework of four-parameter model which are introduced in section 2. Section 3 provides results and discussions of 1073 K for AlMg liquid alloys. Theoretically and experimentally, the measurements of various thermodynamic and microscopic properties were compared. Section 4 outlines the conclusion of the work.

2. Formalism

The integral excess Gibbs free energy of mixing, $G^{XS}_M$ of binary alloy systems in the framework of four-parameter model [22-24] is given by

$$G^{XS}_M = C_A C_B [A_1 + A_2 + A_3 + A_4 + C_A C_B (A_1 + A_2 + A_3 + A_4)]$$

Where $A_1$, $A_2$, $A_3$ and $A_4$ are the interaction energy parameters, $C_A$ and $C_B$ represent the concentrations of the components, A and B respectively of the binary liquid alloy. $R$ and $T$ are the Universal gas constant and absolute temperature of the alloy respectively.

The partial property such as activity coefficient $\gamma_i$ of the component $i (\equiv A, B)$ of binary alloy may be given by

$$RT \ln \gamma_i = G^{XS}_M + (1-C_i) \left( \frac{\partial G^{XS}_M}{\partial C_i} \right)$$

Solution of equation (2) on using equation (1), provides

$$ln \gamma_A = C_A ^2 [A_1 - A_2 + 2 C_B A_3 + C_A (3 C_B - 1) A_3 + 2 C_A C_B (2 C_B - 1) A_4]$$

and

$$ln \gamma_B = C_B ^2 [A_1 + 2 C_B A_2 + C_B (2 - 3 C_B) A_3 + C_B ^2 (3 - 4 C_B) A_4]$$

Again the relation for activity of the component $i (\equiv A, B)$ of the binary liquid alloy may be given by

$$a_i = \gamma_i C_i$$
Now the Gibbs free energy of mixing, $G_M$ of binary liquid alloys is expressed as

$$ G_M = G_M^{XS} + G_M^{id} , \text{ } G_M^{id} = \text{ideal Gibbs free energy of mixing of binary liquid alloy} $$

$$ G_M = G_M^{XS} + RT[C_AlnC_A + C_BlnC_B] $$

$$ \frac{\Delta G}{RT} = C_A C_B [A_1 + C_B A_2 + C_A C_B A_3 + C_B C_B A_4] + C_A lnC_A + C_B lnC_B \quad \text{[using equation (1)]} \quad (6) $$

The partial excess entropy of $i$th component ($i \equiv A, B$) of the binary liquid alloy can be written as

$$ S_i^{XS} = -Rln\gamma_i - RT \left( \frac{\partial ln\gamma_i}{\partial T} \right)_P $$ \quad (7)

On solving (7) by using equations (3) and (4), it can be obtained as

$$ \frac{s_A^{XS}}{R} = -C_B^2 [(A_1 + A_1', T) + (2C_B - 1)(A_2 + A_2', T) + (1 - C_B)(3C_B - 1)(A_3 + A_3', T) + 2C_B(1 - C_B)(2C_B - 1)(A_4 + A_4', T)] \quad (8) $$

and

$$ \frac{s_B^{XS}}{R} = -C_A^2 [(A_1 + A_1', T) + 2C_A(A_2 + A_2', T) + C_A(2 - 3C_A)(A_3 + A_3', T) + C_A^2 (3 - 4C_A)(A_4 + A_4', T)] \quad (9) $$

Where a prime represents the derivative of the interaction parameters $A_1$, $A_2$, $A_3$, and $A_4$ with respect to temperature.

The excess entropy of mixing, $S_M^{XS}$ of the binary liquid alloy is expressed as

$$ \frac{s_M^{XS}}{R} = \frac{s_A^{XS}}{R} + \frac{s_B^{XS}}{R} \quad (10) $$

Again the entropy of mixing, $S_M$ of binary liquid alloy may be expressed as

$$ \frac{s_M}{R} = \frac{s_M^{XS}}{R} + \frac{s_M^{id}}{R} $$

$$ \frac{s_M}{R} = \frac{s_M^{XS}}{R} + C_A lnC_A + C_B lnC_B \quad \text{(11)} $$

The heat of mixing, $H_M$ of binary liquid alloy is given by

$$ H_M = G_M^{XS} - T \left( \frac{\partial G_M^{XS}}{\partial T} \right)_P $$ \quad (12)

Solution of equation (12) on using (1) gives
where a prime represents the derivative of the interaction parameters $A_1$, $A_2$, $A_3$ and $A_4$ with respect to temperature.

Also

$$\frac{H_M}{RT} = g_M^{XS} + \frac{S_M^{XS}}{R}$$  \hspace{1cm} (14)$$

The concentration fluctuations in the long wavelength limit, $S_{CC}(0)$ is correlated to the free energy of mixing, $G_M$ of binary liquid alloy as

$$S_{CC}(0) = Rf\left[\frac{\partial^2 G_M}{\partial C^2}\right]_{T,P,N}^{-1}$$  \hspace{1cm} (15)$$

Solution of equation (15) by using equation (6) provides

$$S_{CC}(0) = [−2A_1 + 2(3C_B − 2)A_2 + 2(1 − 6C_B + 6C_A^2)A_3 + 2(1 − 9C_A + 18C_B^2)
−10C_A^2]A_4 + \frac{1}{C_A C_B}$$  \hspace{1cm} (16)$$

From the measured activity data of binary liquid alloys, $S_{CC}(0)$ can be calculated by means of this relation

$$S_{CC}(0) = C_B a_A \left(\frac{\partial a_A}{\partial C_A}\right)^{-1}_{T,P,N} = C_A a_B \left(\frac{\partial a_B}{\partial C_B}\right)^{-1}_{T,P,N}$$  \hspace{1cm} (17)$$

Based on the above equation, the values computed are considered as experimental values binary liquid alloy.

From the relation above, we can again obtain $S_{CC}^{id}(0)$ of a binary liquid alloy

$$S_{CC}^{id}(0) = C_A C_B$$  \hspace{1cm} (18)$$

The analytical expression for Warren-Cowley short range parameter,$\alpha_i$ [24-25] is given by

$$\alpha_i = \frac{S^{-1}}{S(Z−1)+1}$$  \hspace{1cm} (19)$$

Where $Z$ denotes the coordination number and defined as the nearest neighbors to an atom in a given structure and $S$ is given by

$$S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)}$$  \hspace{1cm} (20)$$

3. Results and Discussions

Different thermodynamic parameters, including excess Gibbs mixing energy,$G_M^{XS}$, Gibbs free energy of mixing , $G_M$, activity of component i(≡Al, Mg), partial excess entropy of component i(≡Al, Mg),
excess entropy of mixing, $S^{XS}_M$, entropy of mixing, $S_M$, enthalpy(heat) of mixing, $H_M$ and microscopic functions like the concentration fluctuations in the long wavelength limit, $S_{CC}(0)$ and Warren-Cowley short range order phenomenon, $\alpha_i$ of AlMg liquid alloys at 1073 K have been computed by means of analytical expressions.

Equation (1) indicates that the computation of $G^{XS}_M$ of AlMg liquid alloys at 1073 K requires the values of interaction parameters $A_1, A_2, A_3$ and $A_4$. In present case, the values of $A_1, A_2, A_3$ and $A_4$ for AlMg liquid alloys at 1073 K have been have been estimated by the least square method on using the calculated values of $G^{XS}_M$ [12] in equation (1). It is to be noted that the interaction parameters $A_1, A_2, A_3$ and $A_4$ are not estimated by the procedure adopted in [22]. Values of the interaction parameters are estimated as

$$A_1 = 1.770, A_2 = 1.134, A_3 = 0.354 \text{ and } A_4 = 0$$

These estimated parameters for AlMg liquid alloys at 1073 K have been utilized to compute $G^{XS}_M$ and $G_M/RT$ from equations (1) and (6) in the whole concentration range from $C_{Al} = 0.1$ to $0.9$ which are presented in figure 1 along with corresponding experimental values [12]. The theoretical and experimental [12] values are in excellent concurrence. Both theoretical and experimental values of $G^{XS}_M/RT$ are minimum i.e. -0.2956 at $C_{Al} = 0.6$. At $= 0.5$, both the theoretical and experimental minimum values of are -0.9718 and -0.9723 respectively. Thus the observed asymmetry in $G^{XS}_M$ and symmetry in $G_M$ of AlMg liquid alloys at 1073 K are well explained by the present theoretical model.

The equations (3) and (4) have been used to compute $\gamma_{Al}$ and $\gamma_{Mg}$ respectively and then equation (5) has been used to find out the values of $a_{Al}$ and $a_{Mg}$ of AlMg liquid alloys at 1073 K throughout the concentration range $C_{Al} = 0.1$ to $0.9$. For consistency same values of interaction parameters have been used. The theoretical and experimental [12] values of $a_{Al}$ and $a_{Mg}$ are in excellent concurrence as evident from figure 1. This provide the confidence in the estimated values of $A_1, A_2, A_3$ and $A_4$.

The computation of $S^{XS}_M$ from equation (10) requires the values of partial entropies of AI and Mg i.e., $S^{Al}_M$ and $S^{Mg}_M$. Further the calculations of $S^{Al}_M$ and $S^{Mg}_M$ from equations (8) and (9) demand the values of $A'_1, A'_2, A'_3$ and $A'_4$ which have been estimated by least square method on using the
experimental data of enthalpy(heat) of mixing $H_M$[12] of AlMg liquid alloys at 1073 K in equation (13). The estimated values are

$$A'_1 = 0.0014823, A'_2 = -0.0004373, A'_3 = 0.0008769 \text{ and } A'_4 = -0.0005694$$

By using equations (8), (9) and (10), the temperature derivatives of $A_1, A_2, A_3 \text{ and } A_4$ values have been used to calculate the excess entropy of mixing in AlMg liquid alloys at 1073 K. The excellent agreement between the theoretical and experimental [12] values of $\frac{S_{SS}}{R}$ has been found as shown in figure 2. The observed asymmetry in $S_M$ of AlMg liquid alloys at 1073 K is well explained by the present theoretical model. The theoretical value of $\frac{S_{SS}}{R}$ is minimum i.e. -0.1060 at $C_{Al} = 0.4$ and minimum experimental values of $\frac{S_{SS}}{R}$ is -0.1057 at the same concentration, $C_{Al} = 0.4$.

Again the theoretical values of $\frac{S_M}{R}$ of AlMg liquid alloys at 1073 K computed on using equation (11) are presented in figure 2 along with experimental values [12]. There is a high degree of agreement between the theoretical and experimental results of $\frac{S_M}{R}$ with their maximum values 0.5932 and 0.5941 respectively at $C_{Al} = 0.5$. Thus the observed symmetry in $S_M$ of AlMg liquid alloy at 1073 K is satisfactorily explained.

The equation (14) has been used to compute the $\frac{H_M}{RT}$ of AlMg liquid alloys at 1073 K. The theoretical and the experimental [12] values are in reasonable agreement as mentioned in figure 2. The minimum values of $\frac{H_M}{RT}$ are -0.3787 (theoretical) and -0.3782 (experimental) both at $C_{Al} = 0.5$. It is necessary to mention that the equation (13) has not been used to compute $\frac{H_M}{RT}$ of AlMg liquid alloy at 1073 K whereas the temperature derivatives of interaction parameters $A_1, A_2, A_3 \text{ and } A_4$ have been estimated on using equation (13).

The concentration fluctuations in the long wavelength limit, $S_{CC}(0)$ of AlMg liquid alloys at 1073 K throughout the concentration range $C_{Al} = 0.1$ to 0.9 has been calculated from equation (16). The
theoretical values of $S_{CC}(0)$ are in well concurrence with the experimental values as shown in figure 3. It is imperative to mention that $S_{CC}(0)$ is a very important microscopic function which explains the interactive nature between the species of the binary liquid alloys. Similarly $S_{CC}(0)<S_{CC}^{id}(0)$ indicates the ordering nature of the binary system with the association of unlike atoms pairing (A-B) as nearest neighbors. In present study, the values of $S_{CC}(0)$ of AlMg liquid alloys at 1073 K are less than $S_{CC}^{id}(0)$ in the entire concentration range from $C_{Al}=0.1$ to 0.9 which exhibit the ordering nature of AlMg liquid alloys at 1073 K with Al-Mg atoms pairing as nearest neighbors. Again the observed asymmetry in $S_{CC}(0)$ is well explained. The maximum values of $S_{CC}(0)$ are 0.1792 (theoretical) and 0.1776 (experimental) both at $C_{Al}=0.4$.

![Figure 3. $S_{CC}(0)$ and $\alpha_1$ of AlMg liquid alloys 1073 K.](image)

The theoretical values of short range order parameter, $\alpha_1$ of AlMg liquid alloys at 1073 K as computed from equation (19) have been presented in figure 3. In the present case, $Z$ is taken to be 10. For characterizing the local arrangement of the atoms in a binary system, the short range order parameter, $\alpha_1$ is very useful. It is well known that $\alpha_1$ varies from -1 to +1 at equiatomic concentration i.e. $C=0.5$. $\alpha_1=-1$ represents the complete ordering in the binary system i.e. preference of compound formation and $\alpha_1=+1$ reveals the segregation in the binary system. The study shows that $\alpha_1$ is negative in the entire concentration range for AlMg liquid alloys at 1073 K and minimum i.e. -0.07 at $C_{Al}=0.7$. This confirms the ordering nature of AlMg liquid alloys at 1073 K.

4. Conclusion

The four-parameter model well explains the thermodynamic and microscopic properties of the compound forming AlMg liquid alloys at 1073 K. Study results indicate that AlMg liquid alloy at 1073 K is weakly interacting in nature and there is a tendency of unlike atoms (Al-Mg) atoms pairing as nearest neighbors indicating that AlMg liquid alloy at 1073 K is an ordered system. The asymmetries in the excess free energy of mixing, $G_{M}^{XX}$, excess entropy of mixing, $S_{M}^{XX}$ and concentration fluctuations, $Scc(0)$ of AlMg liquid alloys at 1073 K are well explained by the present theoretical model. Also the symmetries in free energy of mixing, $G_{M}$, entropy of mixing, $S_{M}$ and heat of mixing, $H_{M}$ of AlMg liquid alloys at 1073 K have been successfully explained. Further the interaction parameters are temperature dependent.
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