ABSTRACT

We have used the complex formation model suggested by Bhatia and Hargrove to study the thermodynamic activity and diffusion coefficient of liquid AlMg alloys. The study of the concentration dependence of the thermodynamic activity throws light on their alloying behaviour. Further, it can be visualized from the study how far the alloys follow Raoultian behaviour and obey Henry’s law. Useful informations have been obtained regarding the glass forming nature of the alloys at 1073 K.

INTRODUCTION

In our previous papers\[2-5\], we have presented the theory of ‘complex formation model’ for the study of the thermodynamic and electronic properties of AlCa, MgZn, CaMg and CuMg alloys in the liquid phase. The present paper is based on the above formalism and has been devoted to the study of diffusion coefficient and concentration dependence of the thermodynamic activity \(a_i\) of the constituents of AlMg alloy. This alloy, like other Mg alloys, is of particular interest due to its commercial application as having glass-forming ability and also it is used in the production and design of light alloys. The study of AlMg alloys throws light on the behavior of their solution. From the nature of \(a_i\) it may be ascertained whether their solution is ideal, non-ideal or a regular solution. Further, we can visualize how far they follow Raoultian behavior and obey Henry’s law; also their tendency for hetero and homocoordination may be predicted.

Thus we have been tempted to study the alloying behavior of this alloy in the liquid state. The work has been initiated with the presumption that Al\(_3\)Mg\(_2\) complex exists in the solid phase. This led theoreticians to assume the existence of chemical complexes or pseudomolecules like \(A_\mu B_\nu\) in the liquid phase as well. On this grown, Bhatia and Singh\[6\] developed a statistical mechanical model for complex forming binary alloys to determine the concentration dependence of their thermodynamic properties.

In the following sections, we have dealt with the formalism, computation and result of the present investigation and finally summarized with the concluding remarks. The computations have been done for the prop-
properties at 1073K as experimental data of some properties are available for comparison.

**FORMALISM**

Let a liquid binary alloy containing in all, $N_A = c_A N$ atoms A and $N_B = c_B N$ atoms B, be assumed to consist of $n_1 N$ free atoms of A, $n_2 N$ atoms of B and $n_3 N$ complexes $A_\mu B_\nu$ which also act as independent scattering centers in the alloy. For the present case of AlMg, $\mu = 3$ and $\nu = 2$. Using conservation of atoms, and setting $N = 1$ in the original Bhatia and Hargrove expression [1], it is possible to write the following equations.

\[
\begin{align*}
n_1 &= 1 - C_B - \mu n_3 \\
n_2 &= C_B - \nu n_3 \\
n &= n_1 + n_2 + n_3
\end{align*}
\]

(1)

Here, $C_A$ and $C_B$ are the concentrations of the first and second species and N is Avogadro’s number.

The volume in which the free atoms are randomly distributed can be expressed as,

\[
\Omega = \Omega_{\text{alloy}} - n_3 N \Omega_c
\]

(2)

Where, $\Omega_{\text{alloy}}$ is the atomic volume of the alloy and $\Omega_c$, the volume of the complex,

\[
W_c = \mu \Omega_1 + \nu \Omega_2
\]

(3)

$\Omega_1$, $\Omega_2$ being the atomic volumes of the first and second species of the alloy, respectively.

The number of complexes $n_3$ at a given temperature and pressure is obtained from the equilibrium condition for the free energy of mixing $G_M$ i.e.

\[
(\partial G_M / \partial n_3)_{T,P,c} = 0
\]

(4)

where, T, P and c represent temperature, pressure and concentration respectively.

$G_M$ for the binary alloy can be written as,

\[
G_M = -n_3 g + \Delta G
\]

(5)

Here g is the formation energy of the complex. The first term in Eq. (5) represents the lowering of the free energy due to the formation of complexes. $\Delta G$ represents the free energy of mixing of the ternary mixture of fixed $n_1$, $n_2$ and $n_3$ whose constituents A, B and $A_\mu B_\nu$ are assumed to be interacting weakly with each other. The strong bonding between the individual elements is taken into account via the formation of the chemical complex. Using $\Delta G$ as originally formulated [1] we can express the free energy of mixing as,

\[
G_M = -n_3 g + RT \sum_{ij} n_i (\ln n_i - \ln n) + \sum_{ij} \sum_{i<j} ((n_i n_j) / n) W_{ij}
\]

(6)

Where, $R$ is the molar gas constant, the $W_{ij}$’s are the interaction energies and by definition they are independent of the concentration although they may depend on temperature and pressure. Eq. (4) and (6) yield

\[
(n_1^2 n_2^2) / (n_3^n) = \exp \left( -g / RT \right) \exp (y_1 + y_2 + y_3)
\]

(7)

Where,

\[
\begin{align*}
y_1 &= (W_{12}/RT) \left[ (\mu + \nu - 1) (n_1 n_2 n^2) - (\mu n_2 n^2) - (\nu n_1 n^2) \right] \\
y_2 &= (W_{13}/RT) \left[ (\mu + \nu - 1) (n_1 n_3 n^2) - (\mu n_3 n^2) - (\nu n_1 n^2) \right] \\
y_3 &= (W_{23}/RT) \left[ (\mu + \nu - 1) (n_2 n_3 n^2) - (\mu n_2 n^2) - (\nu n_2 n^2) \right]
\end{align*}
\]

(8)

The interaction energies $W_{ij}$ and g are determined on the line of Bhatia and Hargrove [7]. Once the energy parameters are selected, they remain the same for all mixing. Eq. (7) is solved numerically to obtain the equilibrium value of $n_3$, which in turn is used in Eq. (6) to evaluate $G_M$ as a function of concentration.

The expression for the Gibbs energy of mixing can then be used to provide an equation for the thermodynamic activity, $a$, using the general relationship,
The thermodynamic activity and diffusion coefficient of liquid AlMg alloys

In the above equation, \( k \) refers to the components A or B, from which one can write as,

\[
\ln a_A = 1 - n + \ln n_1 + \frac{1}{RT} (n_3 w_{13} + n_2 w_{12}) - \frac{1}{RT} \sum_{i<j} n_i n_j w_{ij} (10)
\]

And

\[
\ln a_B = 1 - n + \ln n_2 + \frac{1}{RT} (n_3 w_{12} + n_3 w_{23}) - \frac{1}{RT} \sum_{i<j} n_i n_j w_{ij} (11)
\]

Eq. (10) and (11) can be safely used in conjunction with Eq. (7) to estimate the energy parameters \( W_{ij} \) and \( g \) provided that a good set of data for activities \( a_A \) and \( a_B \) are available from the experiment.

Concentration fluctuation \( S_{cc}(0) \) and chemical diffusion

It is to be mentioned that the activity \( a_A \) and \( a_B \) of the constituent species of the complex forming binary alloy \( A_B \) is involved in the expression of the long wavelength limit (\( S_{cc}(0) \)) of the concentration-concentration structure factor which is consequently used in the computation of the diffusion coefficient of metals \( D_M \) in a complex forming binary alloy. The \( S_{cc}(0) \) computed through the experimental Gibbs free energy of mixing are termed as experimental \( S_{cc}(0) \) obtained through,

\[
S_{cc}(0) = N K_B T \frac{\partial \Delta G_M}{\partial C^2} \biggr|_{T,P,N}^{-1}
\]

\[
= (1 - C) a_A \left( \frac{\partial a_A}{\partial C^2} \right) \biggr|_{T,P,N}^{-1}
\]

\[
= C a_B \left( \frac{\partial a_B}{\partial (1 - C)} \right) \biggr|_{T,P,N}^{-1}
\]

where, \( c \) is the concentration of the first component, \( T,P,N \) are respectively, absolute temperature, pressure and Avogadro’s number.

The ideal value \( S_{cc}^{id}(0) \) is given by,

\[
S_{cc}^{id}(0) = C(1 - C) = C_A C_B
\]

It is possible to use the variation of \( S_{cc}(0) \) with concentration to understand the nature of atomic order in liquid alloys. The basic result is that \( S_{cc}(0) \) < \( S_{cc}^{id}(0) \) implies a tendency for heterocoordination (preference of unlike atoms to pair as nearest neighbours), while \( S_{cc}(0) > S_{cc}^{id}(0) \) implies homocoordination (preference of like atoms as nearest neighbours). For a demixing system \( S_{cc}(0) >> S_{cc}^{id}(0) \). Thus a study of \( S_{cc}(0) \) is quite useful for the understanding of the alloying behaviour. Using the Darken[8] thermodynamic equation for diffusion, one can write,

\[
\frac{D_M}{D_{id}} = \frac{C(1 - C)}{S_{cc}^{id}(0)}
\]

Here, \( D_M \) is the chemical or interdiffusion coefficient and \( D_{id} \) is given as,

\[
D_{id} = C D_B + (1 - C) D_A
\]

where \( D_A \) and \( D_B \) are self diffusion coefficients. It is to be noted that \( D_M/D_{id} \) approaches 1 for ideal mixing, it is greater than 1 for an ordered alloy and is less than 1 for a segregating system. Thus the study of the curves of \( D_M/D_{id} \) throws some light on the alloying behavior of the alloy under investigation.

COMPUTATION AND RESULTS

The values of the energy parameters obtained for AlMg at \( T = 1073 \text{ K} \) are:

\( g/RT = 1.5 \), \( W_{12}/RT = -0.60 \), \( W_{13}/RT = 0.50 \), \( W_{23}/RT = -0.50 \)

Using above interaction parameters, one can use Eq. (7) to obtain numerical value of \( n_3 \) and thus the values of \( n_1 \) and \( n_2 \) using Eq. (1) above. Using the same values of the interaction parameters we show in figure 1. a comparison of the experimental and theoretical values of the activity, it is quite clear that \( a_{Al} \) and \( a_{Mg} \) are matching near \( C_{Mg} = 0.48 \). Both the values are in reasonable agreement.

Figure 1. represents the concentration dependence of the activities of the constituents of AlMg alloy. For Mg constituent it is found that above \( C_{Mg} = 0.8 \) the condition of ideal solution exists i.e. \( a_{Mg} = C_{Mg} \) (Raoultian behaviour). Below this concentration \( a_{Mg} \) is decreasing while \( a_{Al} \) is increasing. A perusal of figure 2 shows that \( D_M/D_{id} \) is different from the ideal value \( D_{id} \). The \( D_M/D_{id} \) curve starts from region of lower concentration, goes on increasing, attains a
maximum at \( C_{\text{Mg}} = 0.4 \). At this concentration \( D_M \) shows the largest departure from its ideal value \( D_{\text{id}} \). After this particular concentration \( D_M/D_{\text{id}} \) goes on decreasing till the other end i.e. \( C_B = 1.0, C_A = 0 \).

**CONCLUSION**

From the above investigation it can be concluded that for AlMg alloy \( S_{cc}(0) < s_{cc}(0) \) at all concentrations and hence the complex formation is expected and the alloy is not glass forming. The concentration fluctuations and the chemical diffusion indicate that the AlMg alloy undergoes a transition from an ordered (Al-rich end) to a segregated (Mg-rich end) state. Most likely cluster which exists in the melt at 1073K is \( \text{Al}_3\text{Mg}_2 \). The concentration dependence of the thermodynamic activity and \( D_M/D_{\text{id}} \) successfully confirms the assumption of \( \text{Al}_3\text{Mg}_2 \) complexes in the melt.

**REFERENCES**