



Thermodynamic activity and diffusion coefficient of liquid AlMg alloys: Complex formation model

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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.

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KEYWORDS

Liquid AlMg alloys;
Thermodynamic activity;
Diffusion coefficient.

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_1 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_1 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_3Mg_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-

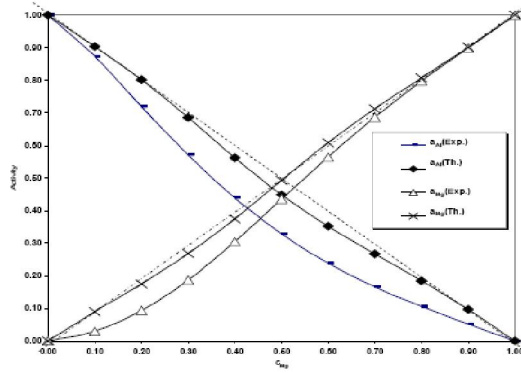


Figure 1 : Concentration dependence of activities at 1073K, Exp.: Experimental, Th. : Theoretical

erties 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.

$$\begin{aligned} n_1 &= 1 - C_B - \mu n_3 \\ n_2 &= C_B - \nu n_3 \\ n &= n_1 + n_2 + n_3 \end{aligned} \quad (1)$$

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,

$$\Omega = \Omega_{\text{alloy}} - n_3 N \Omega_c \quad (2)$$

Where, Ω_{alloy} is the atomic volume of the alloy and Ω_c , the volume of the complex,

$$W_c = \mu \Omega_1 + \nu \Omega_2 \quad (3)$$

Ω_1, Ω_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.

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,c} = 0 \quad (4)$$

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

G_M for the binary alloy can be written as,

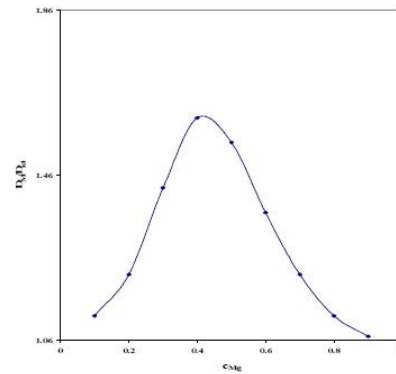


Figure 2 : Computed values of the ratio D_M/D_{id} versus concentration for liquid AlMg alloy

$$G_M = -n_3 g + \Delta G \quad (5)$$

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. ΔG 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 ΔG as originally formulated^[1] we can express the free energy of mixing as,

$$G_M = -n_3 g + RT \sum_{i=1}^3 n_i (\ln n_i - \ln n) + \sum_{i < j} \{(n_i n_j) / n\} W_{ij} \quad (6)$$

Here, 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

$$\frac{(n_1^\mu n_2^\nu)}{(n_3 n^{\mu+\nu-1})} = \exp\left(\frac{-g}{RT}\right) \exp(y_1 + y_2 + y_3) \quad (7)$$

Where,

$$\begin{aligned} y_1 &= (W_{12}/RT) [(\mu+\nu-1) (n_1 n_2 / n^2) - (\mu n_2 / n) - (\nu n_1 / n)], \\ y_2 &= (W_{13}/RT) [(\mu+\nu-1) (n_1 n_3 / n^2) - (\mu n_3 / n) - (n_1 / n)], \\ y_3 &= (W_{23}/RT) [(\mu+\nu-1) (n_2 n_3 / n^2) - (\nu n_3 / n) - (n_2 / n)] \end{aligned} \quad (8)$$

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,

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$$RT \ln a_k = (\partial G_M / \partial N_k)_{T,P,N} \quad (9)$$

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

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

And

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

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 $A_u B_v$ 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,

$$\begin{aligned} S_{cc}(0) &= NK_B T \left(\frac{\partial G_M}{\partial C^2} \right)_{T,P,N}^{-1} \\ &= (1-C) a_A \left(\frac{\partial a_A}{\partial C^2} \right)_{T,P,N}^{-1} \\ &= C a_B \left(\frac{\partial a_B}{\partial (1-C)} \right)_{T,P,N}^{-1} \end{aligned} \quad (12)$$

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,

$$S_{cc}^{id}(0) = C(1-C) = C_A C_B \quad (13)$$

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 $S_{cc}(0) \gg s_{cc}^{id}(0)$. 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,

$$\frac{D_M}{D_{id}} = \frac{C(1-C)}{S_{cc}(0)} \quad (14)$$

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

$$D_{id} = C D_B + (1-C) D_A \quad (15)$$

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 $T = 1073$ 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 $a_{Mg} < C_{Mg}$.

For the Al constituent also we find that from Al end upto $C_{Al} = 0.8$ the condition of ideal solution prevails i.e. $a_{Al} = C_{Al}$. For $C_{Al} < 0.8$ we have $a_{Al} > C_{Al}$ i.e. Mg component shows negative deviation while Al component shows positive deviation from ideal behavior.

A perusal of figure 2 shows that D_M 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 $C_{Mg} = 0.4$. At this concentration D_M shows the largest departure from its ideal value D_{id} . After this particular concentration D_M/D_{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 $S_{cc}(0) < s_{cc}^{id}(0)$ 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 Al_3Mg_2 . The concentration dependence of the thermodynamic activity and D_M/D_{id} successfully confirms the assumption of Al_3Mg_2 complexes in the melt.

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