THERMODYNAMICAL PROPERTIES OF COMPLEX FORMING Al-Mg BINARY ALLOYS

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Some thermo dynamical properties of liquid Al-Mg alloy are investigated with the presumption that a chemical complex of the form Al_3Mg_2 exists near melting. The computed results of free energy of mixing as a function of concentration are in fairly good agreement with the experimental findings.

KEYWORDS : Chemical complex (n_3), free energy of mixing (G_m), heat of formation (H_m), entropy of mixing (S_m).

INTRODUCTION :

In recent past there have been considerable interest in the study of various thermo dynamical properties of liquid binary alloys [1-5]. Very recently Roik *et al* [2] has investigated the specific features of structure factor of binary and ternary liquid alloys of aluminium with 3d-, 4d- transition metals. Few thermo dynamical properties like heat of formation, entropy of mixing, concentration in long wave length limit are computed by Jha *et al* [6].

On the scheme suggested by Bhatia and Hargrove [12, 14], the free energy of mixing (G_m), heat of mixing (H_m) and entropy of mixing (S_m) with the use of equilibrium values of chemical complexes n_3 with the condition $(\delta G_m/\delta n_3)_{T,P,C} = 0$. The comparision wih the experimental results are presented in present paper.

THEORY : COMPLEX FORMATION MODEL

Let a liquid binary alloy containing in all $N_A = (1-C)\,N$ atoms of A and N_B =CN atoms of B be assumed to consists of n_1N free atoms A, n_2N free atoms B and n_3N complexes $A\mu B\nu$ which also acts as independent scattering points in the alloy from conservation of atoms,

$$n_1 = 1-C-\mu n_3$$

$$n_2 = C-\nu n_3$$

$$n = n_1+n_2+n_3$$

$$N_s = n_A+ n_B +n_m = nN$$

Here C is the concentration of the second species B.

The free energy of mixing G_M of the mixture may be written as [Jha *et al* (1990)]

$$G_M = -n_3 g + G^1$$

where g is the formation energy of the complex and thus the first term ($-n_3g$) represents the lowering of the free energy due to the formation of complex in the alloy. G^1 is the free energy of mixing of the ternary mixture of A, B and $A\mu B\nu$. Since strong interactions are taken care of, via the formation of chemical complexes the mixture can be treated as weakly interacting system. Hence, for G^1, the conformal solution approximation [Longuet- Higgins (1951)] can be considered. This enables to express G_M as [Jha *et al* (1990)].

$$G_M = -n_3g + RT \sum_{i=1}^{3} n_j (\ln n_i - \ln n) + \sum \sum_{i<j}^{n_i n_j} \frac{W_{ij}}{n} \quad ...(1)$$

where W_{ij} $(i, j = 1, 2, 3)$ are the interaction energies.

EQUILIBRIUM VALUES OF CHEMICAL COMPLEX FORMULAE:

The equilibrium values of the chemical complex n_3 may be obtained through the condition

$$\left[\frac{\partial G_m}{\partial n_3}\right]_{T,P,C} = 0 \quad ...(2)$$

which gives

$$\frac{n_1^{\mu} n_2^{\upsilon}}{n_3 n^{\mu+\upsilon-1}} = e^{-g/RT} \exp(y_1+y_2+y_3) \quad ...(3)$$

where,

$$y_1 = (w_{12}/RT)\,[(\mu+\nu-1)\,(n_1n_2/n^2) - (\mu n_2/n) - (\nu n_1/n)]$$
$$y_2 = (w_{13}/RT)\,[(\mu+\nu-1)\,(n_1n_3/n^2) - (\mu n_3/n) - (n_1/n)]$$
$$y_3 = (w_{23}/RT)\,[(\mu+\nu-1)\,(n_2n_3/n^2) - (\nu n_3/n) - (n_2/n)] \quad ...(4)$$

This equation can be solved numerically to obtain the equilibrium value of n_3.

The interaction energies W_{ij} are determined following the procedure suggested by Bhatia and Hargrove 1974. At first g is taken nearly equal to $(\mu+w)$ G_M as a starting point and W_{12}, W_{13} and W_{23} are adjusted to get the concentration dependent free energy of mixing through equations (1) & (2). The process is repeated for different sets of energy parameters until a good fit for G_M is obtained. Once the energy parameters have been selected, they remain the same for all mixing all concentrations.

The heat of formation H_M can be obtained through equation (1) and relation.

$$H_M = G_M - T\,(\delta G_M/\delta T)_{PCN} \quad ...(5)$$

On differentiation of equation (1) we get

$$(\delta G_M/\,\delta T) = -n_3\,(\delta g/\,\delta T) + R \sum_{i=1}^{n} n_i\,(\ln n_i - \ln n) + \sum_{i} \sum_{j}^{i=1} (n_i n_j/n)\,(\delta W_{ij}/\,\delta T) \quad ...(6)$$

Putting equations (1) and (6) into (5) yields

$$H_M = -n_3\,[g - T\,(\delta g/\delta T)] + \sum \sum_{i<j} (n_i n_j)\,[W_{ij} - T\,(\delta W_{ij}/\delta T)/n] \quad ...(7)$$

where $\delta g/\,\delta T$ and $\delta W/\,\delta T$ are the temperature dependent energies.

Now entropy of mixing is given by

$$S_M = (H_M - G_M)/T \quad \text{... (8)}$$

COMPUTATION

The free energy of mixing (G_m) is computed from eq. (1), where the interaction energy W_{ij} and have been determined following the procedure suggested by Bhattia and Hargrove (1974). As a starting point g has been taken nearly equal to – (μ+ν) G_m and then the interaction energy W_{12}, W_{13} and W_{23} have been adjusted to get the concentration dependent free energy of mixing through equation (2) and (3). The process has been repeated for different set of energy parameters unit a good fit for G_m is obtained.

Other properties, like heat of mixing (H_m) and entropy of mixing (S_m) have been calculated from eq. (7) and (8), respectively. The computed research of G_M, are presented in Table – 1 and the result of H_m and S_m presented in table – 2.

RESULTS AND DISCUSSION

EQUILIBRIUM VALUE OF CHEMICAL COMPLEX (n_3) AND

FREE ENERGY OF MIXING (G_m) OF LIQUID Al_3Mg_2 ALLOY

(Al_3Mg_2)

Chemical Complex

$$\mu Al_3 + \nu Mg_2 = Al_\mu Mg_\nu$$

$$\mu = 3 \qquad \nu = 2$$

Interaction Energy at $T = 1073°$ K

$$g/RT = 2.0$$

$$W_{12}/RT = -0.9$$

$$W_{13}/RT = -0.5$$

$$W_{23}/RT = -0.4$$

Table-1

C	n_3	G_m	
		Theoretical	**Experimental**
0.1	0.0055736	–0.4177	–0.472
0.2	0.017063	–0.6804	–0.7385
0.3	0.028	–0.8584	–0.8952
0.4	0.032274	–0.9557	–0.9689
0.5	0.02786	–0.9752	–0.9722
0.6	0.018694	–0.9265	–0.9145
0.7	0.0095095	–0.8186	–0.8009
0.8	0.003139	–0.6504	–0.6297
0.9	0.00039044	–0.4068	–0.3899

HEAT OF FORMATION (H_m) AND

ENTROPY OF MIXING (S_m) OF LIQUID Al_3Mg_2 ALLOY (Al_3Mg_2)

$g/RT = 2.0$ $Dg/RT = 2.0$

$W_{12}/RT = -0.9$ $DW_{12}/RT = 0.62$

$W_{13}/RT = -0.5$ $DW_{13}/RT = 3.5$

$W_{23}/RT = -0.4$ $DW_{23}/RT = 4.5$

Table–2

C	N_3	H_m		S_m	
		Theoretical	**Experimental**	**Theoretical**	**Experimental**
0.1	0.0055736	–0.14141	–0.1464	0.2763	0.3257
0.2	0.017063	–0.2537	–0.2604	0.4266	0.4778
0.3	0.028	–0.3309	–0.3373	0.5274	0.5578
0.4	0.032274	–0.3745	–0.3768	0.58113	0.592
0.5	0.02786	–0.3882	–0.3782	0.58764	0.5941
0.6	0.18694	–0.3713	–0.3472	0.5554	0.5674
0.7	0.0095095	–0.323	–0.2881	0.4955	0.5125
0.8	0.003139	–0.2445	–0.206	0.4058	0.4234
0.9	0.00039044	–0.13696	–0.1079	0.2698	0.2819

OBSERVATION

The investigated values of number of complexes (n_3) and free energy of mixing (G_m) are plotted in fig. 1. The experimental values [22] are also depicted in the fig. Our calculated values are found in fairly good agreement with the experiment. The computed values of heat of mixing (H_m) and entropy of mixing S_m are plotted in figure 2. The computed results H_m and S_m are in good agreement with the experimental findings.

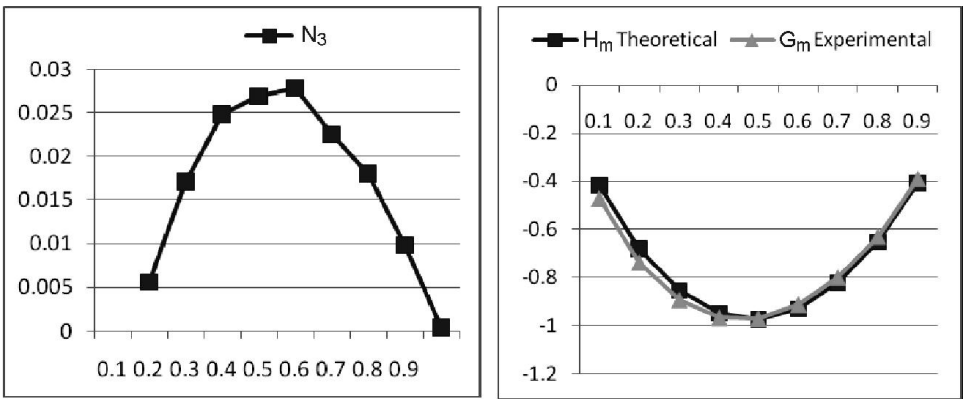

Fig. 1

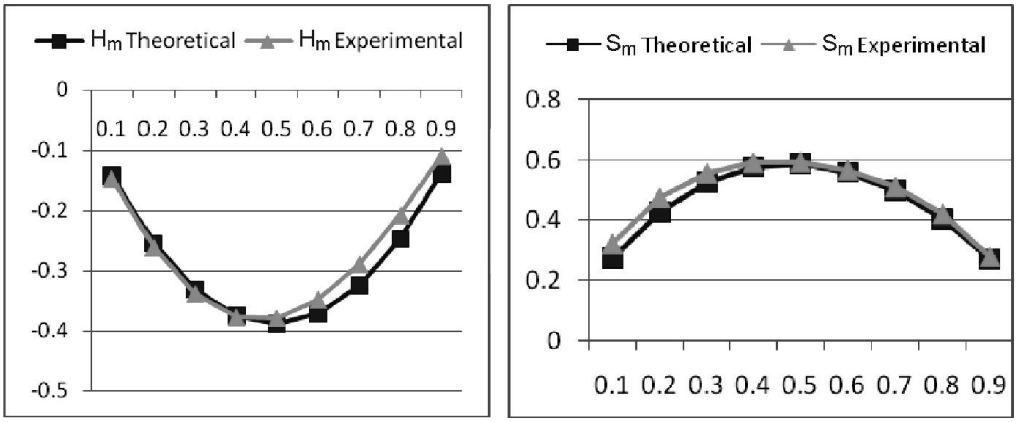

Fig. 2

Conclusion

In the present paper, for the study, the number of complexes (n_3) is found maximum around the stoichiometric composition in the liquid binary alloy. Free energy of mixing in the liquid alloys considered here for the study is the asymmetric about $C = 0.5$. The thermo dynamical properties calculated here for Al_3Mg_2 are in well agreement with experimental.

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