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THERMODYNAMICAL PROPERTIES OF COMPLEX FORMING AL- Zn BINARY ALLOYS

ANIL KUMAR, M.M. KHAN, S.K. MANDAL

P.G. Dept. of Physics, T.M. Bhagalpur University, Bhagalpur-812007, (Bihar), India

AND

S.M. RAFIQUE

Retd. Prof. and Head, P.G. Dept. of Physics, T.M. Bhagalpur University, Bhagalpur-812007, (Bihar), India

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In the present paper the theoretical study of some thermal properties of aluminium based binary alloys have been presented. The calculation of free energy of mixing (G_m), Heat of formation (H_m) and entropy (S_m) are calculated on the scheme suggested by Bhatia and Hargrove. The agreement between theory and experiment are found quite well.

KEYWORDS : Chemical complex (n_3), free energy of mixing (Gm), heat of formation (Hm), entropy of mixing (Sm).

Introduction

The characteristics behaviour of liquid binary alloys have been of long standing interest to theoreticians. Recently the specific features of structure factor of binary and ternary liquid alloys of aluminium with 3d-, 4d-transition metals are demonstrated by Roik *et al*. The alloying behaviour of Al-Ca has been investigated, which are used to compute some thermodynamical properties of liquid binary alloys. Thermodynamic and surface properties of liquid binary alloys are presented by Akinlade .

Energy of liquid metals are easily computable within the frame work of psedopontial theory (Harrison 1966 & Faber 1972) which enables one to write down the energy terms of the psedopontial and structure factor. This can easily be extended for the calculation of the total energy of the binary liquids alloys.

In the present paper, we have investigated some thermodynamic properties, such as free energy of mixing (Gm), heat of mixing (Hm) and entropy of mixing (Sm) 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 computed values of Gm, Hm and Sm are in well agreement with the experimental findings. The theory successfully explains the composition dependent asymmetry of the thermodynamic functions. For Al-Zn alloy, Gm/RT is found greater than and equal to 2.8 shows strong interacting system.

Theory : Complex formation model [Bhatia and Hargrove (1974), Bhatia (1977), Singh(1987), Jha *et al* (1990), Singh *et al* (1993), Mishra *et al* (1994), Jha *et al* (2000, 2001)] assumes the liquid binary alloy *A-B* as a ternary mixture consisting of free atoms *A*, free atoms B and their preferential association, referred as chemical complex or pseudo molecule $A\mu B\nu$.

Let us suppose that there are n_A (= n_1N) of free atoms A, n_B (= n_2N) of free atoms B and n_m (= n_3N) number of chemical complexes exist in the mixture. Then the total member of scattering points is

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

where N is the total number of atom A and atom B

i.e., $N = N_A + N_B$

and $n = n_1 + n_2 + n_3$

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

$n_2 = C - \nu n_3$

Here C is the concentration of the second component.

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)].

$$G_M = -n_3 g + RT\sum_{i=1}^{3} n_j(\ln\ n_i - \ln\ n) + \sum_{i<j}\sum^{n_i n_j} \frac{W_{ij}}{n} \qquad \dots (1)$$

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

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

which gives

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

where,

$$y_1 = (w_{12}/RT)\,[(\mu + \nu - 1)\,(n_1n_2/n^2) - (\mu n_2/n) - (\nu n_1/n)]$$

$$y_2 = (w_{13}/RT)\,[(\mu + \nu - 1)\,(n_1n_3/n^2) - (\mu n_3/n) - (n_1/n)]$$

$$y_3 = (w_{23}/RT)\,[(\mu + \nu - 1)\,(n_2n_3/n^2) - (\nu n_3/n) - (n_2/n)] \qquad \dots (4)$$

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) and (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.

COMPUTATION

In the chemical equilibrium equation ($\mu_A + \nu_B \Leftrightarrow A_\mu B_\nu$), μ and ν play an important role. The asymmetry is pronounced at or around the complex forming concentration C_2 (= 1 – μ/(μ + ν)), the work has been initiated with the presumption that the complex Al_2Zn_3 exists in liquid Al-Zn. The intraction energy W_{ij} and g have been determined following the procedure suggested by Bhattia and Hargrove (1974), g has been taken nearly equal to – (μ + ν) Gm as a starting points and then the interaction energy W_{12}, W_{13} and W_{23} have been adjusted to yet 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 Gm is obtained.

RESULTS AND DISCUSSION

EQUILIBRIUM VALUE OF CHEMICAL COMPLEX (n_3)

AND

FREE ENERGY OF MIXING (Gm) OF LIQUID AL_2Zn_3 ALLOY

(AL_2Zn_3)

Chemical Complex

$\mu Al_2 + \nu Zn_3 = Al_\mu Zn_\nu$

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

Interaction Energy at $T = 1000°$ K

$g/RT = 2.50$

$W_{12}/RT = 1.30$

$W_{13}/RT = – 5.07$

$W_{23}/RT = – 5.642$

C	n_3	Gm	
		Theoretical	**Experimental**
0.1	0.0014401	– 0.2243	– 0.2527
0.2	0.0050162	– 0.3496	– 0.3685
0.3	0.0083045	– 0.4334	– 0.4375
0.4	0.01038	– 0.4814	– 0.4793
0.5	0.0112	– 0.4993	– 0.4984
0.6	0.010907	– 0.49	– 0.4914
0.7	0.009494	– 0.4513	– 0.4536
0.8	0.00679	– 0.3744	– 0.3756
0.9	0.002911	-0.2436	-0.2477

HEAT OF FORMATION (Hm)

AND

ENTROPY OF MIXING (Sm) OF LIQUID AL_2Zn_3 ALLOY

(AL_2Zn_3)

$g/RT = 2.5$ $\quad$ $Dg/RT = 1.0$

$W_{12}/RT = 1.30$ $\quad$ $DW_{12}/RT = -0.40$

$W_{13}/RT = -5.07$ $\quad$ $DW_{13}/RT = -0.20$

$W_{23}/RT = -5.642$ $\quad$ $DW_{23}/RT = -0.52$

C	N_3	H_m		S_m	
		Theoretical	**Experimental**	**Theoretical**	**Experimental**
0.1	0.0014401	0.13676	0.1133	0.36111	0.366
0.2	0.0050162	0.21681	0.1989	0.56644	0.5674
0.3	0.0083045	0.26779	0.2598	0.70119	0.6973
0.4	0.01038	0.29876	0.296	0.7802	0.7753
0.5	0.0112	0.30907	0.3091	0.80835	0.8075
0.6	0.10907	0.29657	0.299	0.78654	0.7904
0.7	0.009494	0.26091	0.2648	0.71218	0.7179
0.8	0.00679	0.20361	0.2049	0.578	0.5805
0.9	0.002911	0.1237	0.1178	0.36731	0.3655

OBSERVATION

In figure-1, the computed values of number of complexes (n_3) and free energy of mixing (Gm) are plotted. The experimental values of Gm are also shown in the figure. From figure-1, it is observed that the number of complexes is found maximum at the composition 0.5. The maximum value of Gm is found at composition 0.5. the experimental values of Gm are in fairly good agreement with the experimental value of Hultgren *et al* [ ].

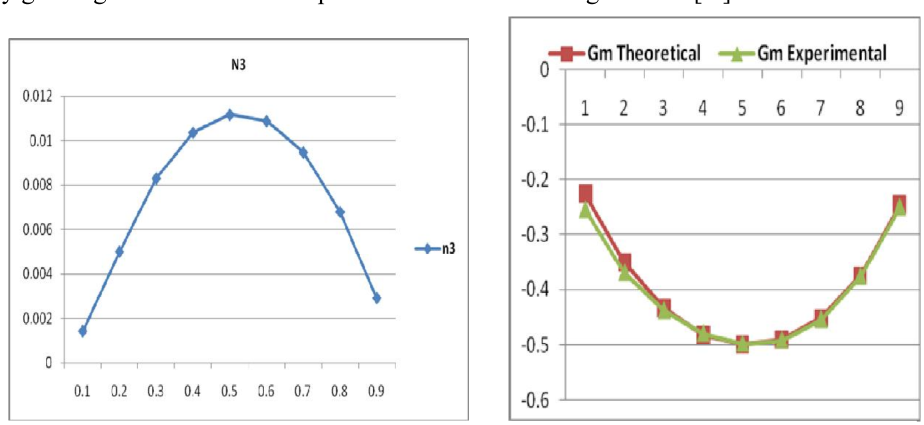

Fig. 1

The computed values of heat of formation Hm and energy of mixing Sm are shown in figure 2 along with their experimental findings. Figure 2 shows, there is an excellent agreement between the theoretical and experimental values [ ] of heat of formation (Hm). There is also well agreement between theory and experiment in case of entropy of mixing (Sm).

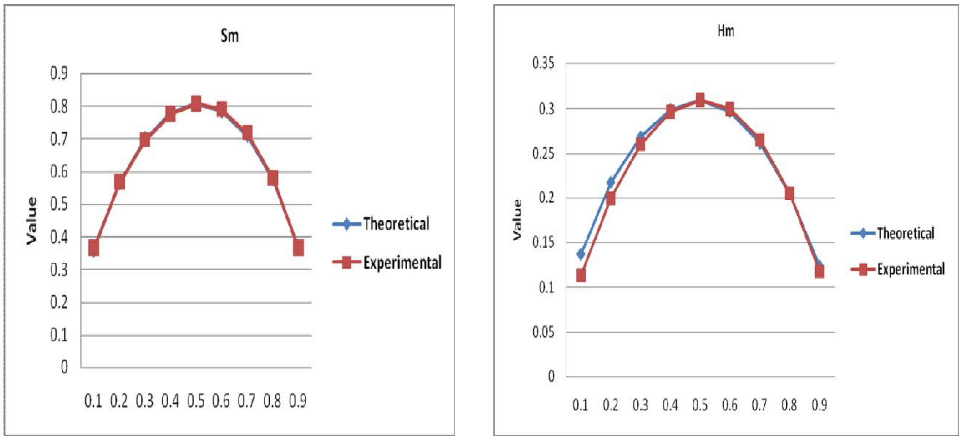

Fig. 2

Conclusion

The value of number of complexes (n_3) is maximum around the stoichiometric composition in the liquid alloy consider here for the study. Free energy of mixing in the liquid alloys considered here for the study is the asymmetric about C = 0.5. The computed values of n_3, Gm & Hm, in the case of AlFe are in fairly good agreement with experimental values.

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