

## THERMODYNAMICAL PROPERTIES OF COMPLEX FORMING Al-Fe BINARY ALLOYS

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In the present paper the theoretical study of some thermal properties of aluminium based binary alloys has 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 ( $G_m$ ), heat of formation ( $H_m$ ), entropy of mixing ( $S_m$ )

### 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 thermo dynamical 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 pseudopotential theory (Harrison 1966 & Faber 1972) which enables one to write down the energy terms of the pseudopotential 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 ( $G_m$ ), 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 computed values of  $G_m$ ,  $H_m$  and  $S_m$  are in well agreement with the experimental findings. The theory successfully explains the composition dependent asymmetry of the thermodynamic functions.

### 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 number 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)]

$$G_M = -n_3g + G^1$$

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)].

$$G_M = -n_3g + RT \sum_{i=1}^3 n_j (\ln n_i - \ln n) + \sum_i \sum_j \frac{n_i n_j W_{ij}}{n} \quad \dots(1)$$

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

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

which gives 
$$\frac{n_1^\mu n_2^\nu}{n_3 n^{\mu+\nu-1}} = e^{-g/RT} \exp(\gamma_1 + \gamma_2 + \gamma_3) \quad \dots(3)$$

where, 
$$\begin{aligned} \gamma_1 &= (w_{12}/RT) [( \mu + \nu - 1 ) ( n_1 n_2 / n^2 ) - ( \mu n_2 / n ) - ( \nu n_1 / n )] \\ \gamma_2 &= (w_{13}/RT) [( \mu + \nu - 1 ) ( n_1 n_3 / n^2 ) - ( \mu n_3 / n ) - ( n_1 / n )] \\ \gamma_3 &= (w_{23}/RT) [( \mu + \nu - 1 ) ( n_2 n_3 / n^2 ) - ( \nu n_3 / n ) - ( n_2 / n )] \end{aligned} \quad \dots(4)$$

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  $(\mu + \nu) G_M$  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.

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

On differentiation of equation (1) we get

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

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

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

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

Now entropy of mixing is given by

$$S_M = (H_M - G_M) / T \quad \dots(8)$$

## COMPUTATION :

In the chemical equilibrium equation ( $\mu_A + \nu_B \Leftrightarrow A_\mu B_\nu$ ),  $\mu$  and  $\nu$  play an important role. The asymmetry is pronounced at or around the complex forming concentration  $C_2$  ( $=1 - \mu / (\mu + \nu)$ ), the work has been initiated with the presumption that the complex  $Al_3Fe$  exists in liquid Al-Fe. The interaction energy  $W_{ij}$  and  $g$  have been determined following the procedure suggested by Bhattia and Hargrove (1974),  $g$  has been taken nearly equal to  $-(\mu + \nu) G_m$  as a starting points 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 until a good fit for  $G_m$  is obtained.

## RESULTS AND DISCUSSION :

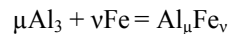
### EQUILIBRIUM VALUE OF CHEMICAL COMPLEX ( $n_3$ )

AND

### FREE ENERGY OF MIXING ( $G_m$ ) OF LIQUID $Al_3Fe$ ALLOY

(  $Al_3Fe$  )

Chemical Complex



$$\mu = 3 \quad \nu = 1$$

Interaction Energy at  $T = 1873^\circ K$

$$g/RT = 6.0$$

$$W_{12}/RT = -0.7$$

$$W_{13}/RT = -0.6$$

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

**Table- 1**

| C   | $n_3$   | $G_m$       |              |
|-----|---------|-------------|--------------|
|     |         | Theoretical | Experimental |
| 0.1 | 0.03296 | -0.6355     | -0.6376      |
| 0.2 | 0.0585  | -1.0343     | -1.0353      |
| 0.3 | 0.090   | -1.3464     | -1.2875      |
| 0.4 | 0.109   | -1.419      | -1.4196      |
| 0.5 | 0.122   | -1.4373     | -1.4196      |
| 0.6 | 0.105   | -1.2463     | -1.3774      |
| 0.7 | 0.073   | -1.0058     | -1.2163      |
| 0.8 | 0.042   | -0.7318     | -0.9574      |
| 0.9 | 0.015   | -0.4184     | -0.5817      |

HEAT OF FORMATION ( $H_m$ )

AND

ENTROPY OF MIXING ( $S_m$ ) OF LIQUID  $Al_3Fe$  ALLOY(  $Al_3Fe$  )

$$g/RT = 6.0$$

$$Dg/RT = 1.5$$

$$W_{12}/RT = -0.7$$

$$DW_{12}/RT = 2.2$$

$$W_{13}/RT = -0.6$$

$$DW_{13}/RT = 1.6$$

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

$$DW_{23}/RT = 1.0$$

**Table - 2**

| C   | $N_3$   | $H_m$       | $S_m$       |
|-----|---------|-------------|-------------|
|     |         | Theoretical | Theoretical |
| 0.1 | 0.03296 | -0.36525    | 0.27026     |
| 0.2 | 0.0585  | -0.61148    | 0.42282     |
| 0.3 | 0.090   | -0.77847    | 0.567901    |
| 0.4 | 0.109   | -0.80135    | 0.63102     |
| 0.5 | 0.122   | -0.80655    | 0.64673     |
| 0.6 | 0.105   | -0.68692    | 0.55935     |
| 0.7 | 0.073   | -0.55287    | 0.45292     |
| 0.8 | 0.042   | -0.40307    | 0.32869     |
| 0.9 | 0.015   | -0.22906    | 0.18936     |

## OBSERVATION

In figure-1, the computed values of number of complexes ( $n_3$ ) and free energy of mixing ( $G_m$ ) are plotted. The experimental values of  $G_m$  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  $G_m$  is found at composition 0.5. The experimental values of  $G_m$  are in fairly good agreement with the experimental value of Hultgren *et al* [24].

The computed values of heat of formation  $H_m$  and energy of mixing  $S_m$  are shown in figure-2 along with their experimental findings. Figure-2 shows, there is an excellent agreement between the theoretical and experimental values [24] of heat of formation ( $H_m$ ). There is also well agreement between theory and experiment in case of entropy of mixing ( $S_m$ ).

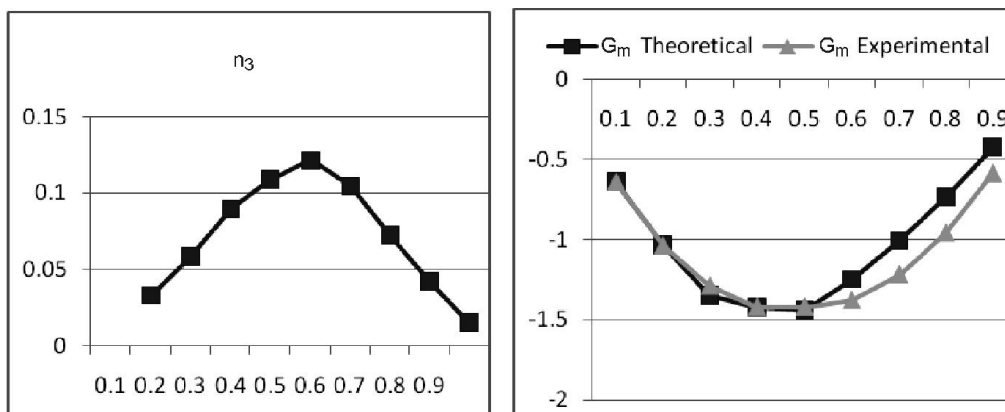


Fig. 1

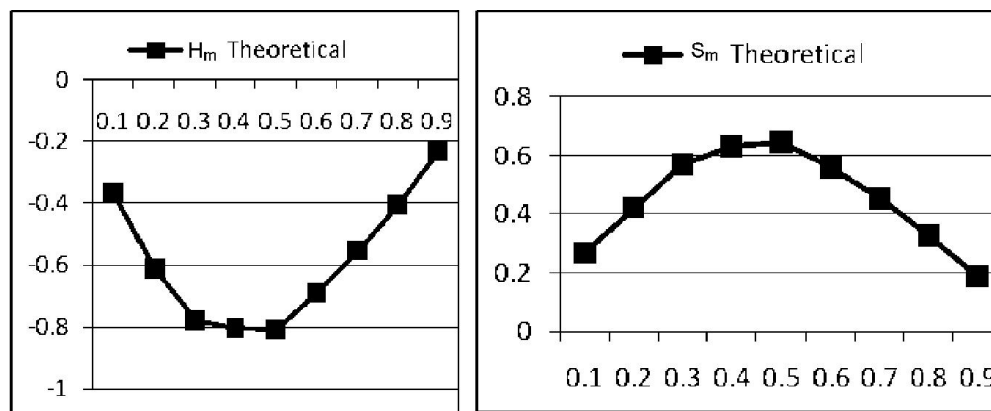


Fig. 2

## 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  $G_m$ ,  $H_m$  &  $S_m$  in the case of  $Al_3Fe$  are in fairly good agreement with experimental values.

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