STUDY OF SEGREGATING NATURE IN LIQUID Al-Ga ALLOYS

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Abstract:We report energetic of mixing behavior of liquid Al-Ga alloys, using simple statistical theory through concentration dependence thermodynamic, structural, transport and surface properties at 1023K. The concentration dependent thermodynamic functions (free energy of mixing, enthalpy of mixing, entropy of mixing and activity coefficient of the component), structural functions (concentration fluctuation in the long wavelength limit and chemical short range order parameter), transport properties (diffusivity and viscosity) and surface properties (surface segregation and surface tension) have got special attention to show a tendency of homo-coordination of atom in the mixture. The theoretical analysis reveals that input parameter, order energy is temperature dependent and Al-Ga alloys is of weakly interacting system.

Keywords: Simple statistical theory; Liquid alloy; Order energy; Structural functions; Surface segregation.

INTRODUCTION

Liquid alloys are disorder system with short range order and exhibit a significant variety of atomic structures. The various properties of the alloys in the melt are helpful to understand the alloying behaviour in the solid state which is of immense important in metallurgical science for preparing metal alloys. Due to the strong correlation among the atoms and their state of disorder, the formulation of exact theory of liquid alloy to understand thermodynamic and structural properties, arises a problem of mathematical complexity. It is much more difficult to understand the properties of disordered material like liquid alloys as compared to those of crystal (Adhikari et al.2012). Many experimentalists (Hultgren et al. 1973; Saboungi et al.1978; Lamparter et al.1984; Harada et al.1988; Iida & Guthrie,1988) as well as theoreticians (Flory, 1942; Lebowitz, 1964; Harrision, 1966; Faber, 1972; Bhatia et al. 1973; Shimoji, 1977; Alonso & March, 1982; Bernu et al. 1987; Singh, 1987; Li & Tosi, 1989; Singh et al. 1990, 1993; Anusionwu, 2002; Novakovic, 2010; Adhikari et al.2012; Koirala et al. 2013) have long been trying to interpret the alloying nature of liquid alloys. The concentration dependent properties of liquid alloys, basically thermodynamic and structural, can provide enormous amount of information for understanding metallurgical process and material preparation of the metal alloys. Thermodynamic properties help to know the stability and bonding strength of different constituents in the alloys. The structural properties are useful in obtaining the microscopic information on structure of molten alloys. The ordering and phase separation behavior of molten alloys and the nature of transition from fluid phase to the glassy state can be explained on the basis of these structural functions.

In metallurgical science, metal alloys are generally beneficial over metals for their increased mechanical strength, heat resistance, chemical resistance, and decreased production costs. Aluminium and aluminium alloys have many outstanding attributes that lead to a wide range of applications, including good corrosion and oxidation resistance, high electrical and thermal conductivities, low density, high reflexivity, high ductility and reasonably high strength and relatively low cost. Aluminium alloys are non-toxic and easiest to recycle among the structural materials (Campbell 2008). Aluminium has a large negative free energy with strong oxide formation capacity. It, therefore, has thermodynamic ability to split water. The liquid Al-Ga alloys spontaneously produce hydrogen if mixed with water. This technology could be used to generate hydrogen on demand and hence unnecessary storage of hydrogen is not required (Woodall 2007).

In the present work we intend to explain the alloying behavior of aluminium-gallium liquid on the basis of simple statistical model. It is a statistical mechanical model in which the grand partition function is used to obtain analytical expressions for the conditional probabilities enumerating the occupation of two neighbouring sites by the atoms of the constituent elements in terms of the ordering energy (Singh et al.1990). The ordering energy, an important input parameter, is used for all calculations which is temperature dependent. The observed thermodynamic

properties of mixing (free energy of mixing, enthalpy of mixing and entropy of mixing) of Al-Ga alloys at 1023K are symmetrical about equiatomic composition (Hultgren et al.) and the value of concentration fluctuation in long wavelength limit which is calculated from the activity data (Hultgren et al.) shows that the alloys is segregating in nature even though atomic mismatch (V_{Ga}/V_{Al} = 1.18) and electronegativity difference (=0 .20) are not significantly large.

Paper outlines are as follows: In section 2, general formalism about the theory is presented. Section 3 deals with the result and discussion and conclusion are presented in section 4.

METHODOLOGY

In the simple statistical model a grand partition function is constructed to deduce the relation for thermodynamic and structural functions.

Thermodynamic functions

The grand partition function for simple binary liquid alloys consisting of $N_A(=Nc)$ number of A atoms and $N_B(=N(1-c))$ number of B atoms can be generalized as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp\left(\frac{\mu_A N_A + \mu_B N_B - E}{k_B T}\right) \quad (1)$$

Where $q_i^{N_i}$ are the partition functions of atoms (i=A or B) associated with inner and vibrational degree of freedom. q_i the same whether the atom i is located in the pure state or in alloy. μ_A and μ_B are the chemical potentials and E is the configurational energy, k_B, the Boltzmann constant, c, the concentration of the component and T, absolute temperature (Singh et al.1990). The standard thermodynamic relation for free energy of mixing is

$$G_M = G_M^{id} + G_M^{XS} \quad (2)$$

where

$$G_M^{id} = RT\{c\ln c + (1-c)\ln(1-c)\} \quad (3)$$

And

$$G_M^{XS} = \int_0^c \ln\sigma^z dc \quad (4)$$
$$= RT\{c\ln\gamma_A + (1-c)\ln\gamma_B\}$$
with

$$\sigma = (\beta + 2c - 1)\exp(-\omega/zk_B T)/2c \quad 4(a)$$

$$\gamma_A = [(\beta - 1 + 2c)/c(1+\beta)]^{z/2} \quad 4(b)$$

$$\gamma_B = [(\beta + 1 - 2c)/(1-c)(1+\beta)]^{z/2} \quad 4(c)$$

$$\beta = \{1 + 4c(1-c)[\exp(2\omega/zk_B T) - 1]\}^{1/2} \quad 4(d)$$

For the equiatomic composition ($c = \frac{1}{2}$), relation (4) reduces to

$$\frac{G_M^{XS}}{RT} = \ln 2^{z/2}[1 + \exp(-\omega/zk_B T)]^{-z/2} \quad (5)$$

Using the relations (2),(3) and (4), the free energy of mixing will be

$$G_M = RT[c\ln c + (1-c)\ln(1-c) + c\ln\gamma_A + (1-c)\gamma_B]$$
$$= RT[c\ln c + (1-c)\ln(1-c) + c(1-c)\frac{\omega}{k_B T}] \quad (6)$$

The heat of mixing (H_M) can be obtained from the standard thermodynamic expression as

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{C,P,N}$$
$$= RT[c(1-c)\frac{\omega}{k_B T} - c(1-c)\frac{1}{k_B}\frac{d\omega}{dT}] \quad (7)$$

and entropy of mixing (S_M) is also obtained from the relation

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

The activity of binary liquid alloys, a_i (i=A or B) , can be related to the free energy of mixing by the relation

$$RT\ln a_i = G_M + (1-c_i)\left(\frac{\partial G_M}{\partial c_i}\right)_{T,P,N} \quad (9)$$

Then we have from Eq. (6),

$$\ln a_A = \ln c + (1-c)^2 \frac{\omega}{k_B T} \quad 9(a)$$

$$\ln a_B = \ln(1-c) + c^2 \frac{\omega}{k_B T} \quad 9(b)$$

Structural Properties

Concentration fluctuations in the long wavelength limit ($S_{cc}(0)$) is an essential structural function which has been widely used to study the nature of atomic order in binary liquid alloys (Bhatia et al.1973). $S_{cc}(0)$ is thermodynamically related to experimental activity of each component by the standard relations given as

$$S_{cc}(0) = (1-c)\left(\frac{\partial \ln a_A}{\partial c}\right)^{-1} \quad (10)$$

$$= c\left(\frac{\partial \ln a_B}{\partial(1-c)}\right)^{-1} \quad (11)$$

Theoretically $S_{cc}(0)$ can be evaluated from eq.(6) through standard relation given below

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial c^2} \right)_{T,P,N}^{-1}$$

$$= c(1-c) \left[1 + \frac{z}{2\beta}(1-\beta) \right]^{-1} \quad (12)$$

When the ordering energy is zero, Eq.(12) reduces to

$$S_{cc}(0) = c(1-c) = S_{cc}(0, id) \quad (13)$$

Owing to difficulties in diffraction experiments, the theoretical determination of $S_{cc}(0)$ is of great importance when the nature of atomic interactions in the melt has to be analysed. The mixing behaviour of liquid alloys can be deduced from the deviation of $S_{cc}(0)$ from the ideal value, $S_{cc}(0,id)$. $S_{cc}(0) < S_{cc}(0,id)$ indicates that the chemical order prefers hetero-pairs, whereas if $S_{cc}(0) > S_{cc}(0,id)$, the chemical order leads to a preference of homo-pairs.

Chemical short range order parameter α_1 is another important structural function, which gives insight into the local arrangement of the atoms in the molten alloys (Cowley 1950,Warren 1969). It is difficult to obtain the experimental values of α1 , because of difficulties in diffraction experiment but theoretical values of this parameter are easily obtain via conditional probability [A/B] which defines the probability of finding an A-atom as a nearest neighbor of a given B-atom (Cowley 1950,Warren 1969). To quantify the degree of order in the molten alloys α_1 can be evaluated theoretically:

$$\frac{S_{cc}(0)}{c(1-c)} = \frac{1+\alpha_1}{1-(z-1)\alpha_1} \quad (14)$$

where z is the coordination number, which is taken as 10 for our purposes. We note that varying the value of z does not have any effect on the position of the minima of α_1. The knowledge of the CSRO parameter provides an immediate insight into the nature of the local arrangement of atoms in the mixture. For the equiatomic composition, the CSRO parameter is found to be $-1 \leq \alpha_1 \geq 1$. The negative values of α_1 indicate ordering in the melt, which is complete if $\alpha_1 = -1$. On contrary, positive values of α_1 indicate segregating, leading to phase separation if $\alpha_1 = 1$.

Transport properties

The transport properties such as viscosity, chemical diffusion coefficients etc may help to gain knowledge about the mixing behaviour of binary liquid alloys at the microscopic level. Viscosity (η) of liquid alloys is equally important in the understanding of the atomic level structure and interactions. As in the case of thermodynamic functions, the composition dependence of viscosity of liquid alloys is also found to exhibit either a linear variation, or positive or negative

deviations from the linear law. A simple formula for the investigation of viscosity of a binary solution is

$$\eta = \eta_{id} \left[1 - c(1-c) \left(\frac{2\omega}{k_B T} \right) \right] \quad (15)$$

But, $\quad \eta_{id} = c\eta_A^0 + (1-c)\eta_B^0 \quad (16)$

where η_i^0 is the viscosity of pure component i (i= A,B); ω is the interchange energy or order energy; c, the concentration of the component; kB,T are Boltzmann constant and absolute temperature(MoelevynHughes,1964).

The mixing behaviour of the alloy forming molten metals can also be studied at the microscopic level in terms of coefficient of diffusion. The mutual diffusion coefficient (D_M) of binary liquid alloys can be expressed in terms of activity (f_i) and intrinsic diffusion coefficient (D_{id}) of an ideal mixture with the help of Darken's equation (Darken, 1953).

$$\frac{D_M}{D_{id}} = \frac{d \ln f_i}{dx_i} \quad (17)$$

Considering only the energetics of the nearest- neighbour bond, we obtain an expression for

$$D_M \quad \frac{D_M}{D_{id}} = \left[1 - c(1-c) \left(\frac{2\omega}{k_B T} \right) \right] \quad (18)$$

with $\quad D_M = c\, D_B + (1-c)\, D_A \quad (19)$

where D_A and D_B are the self-diffusion coefficients of pure components A and B respectively.

The ratio D_M / D_{id} indicates the mixing nature of molten alloys; $D_M / D_{id} < 1$ indicates the tendency of homo-coordination while $D_M / D_{id} > 1$ indicates the tendency of hetero-coordination and D_M / D_{id} approaches 1 for ideal mixing.

Surface properties

For the processing of materials and productions in the metallurgical industry, knowledge of surface phenomena like surface segregation and surface tension is essential. On the basis of assumption of monatomic surface layer, Butler's approach (Butler, 1932) of surface tension τ of liquid solution can be expressed as

$$\tau = \frac{\mu_A^s - \mu_A^b}{\alpha_A} = \frac{\mu_B^s - \mu_B^b}{\alpha_B} = \ldots\ldots = \frac{\mu_i^s - \mu_i^b}{\alpha_i} \quad (20)$$

Where μ_i^s, μ_i^b and α_i represent respectively the chemical potential in the hypothetical surface and that in the bulk and molar surface area of pure component i (A or B).

Equation(20) yields the expressions for surface tension in terms of partial excess free energy of mixing in bulk($G_i^{E,b}$) and at the surface($G_i^{E,s}$) and concentration in the bulk(c) and at the surface(c^s) as

$$\tau = \tau_A + \frac{1}{\alpha_A}\left(G_A^{E,s} - G_A^{E,b}\right)$$

$$+ \frac{RT}{\alpha_A}\ln c^s - \frac{RT}{\alpha_A}\ln c \qquad 21(a)$$

$$\tau = \tau_B + \frac{1}{\alpha_B}\left(G_B^{E,s} - G_B^{E,b}\right)$$

$$+ \frac{RT}{\alpha_B}\ln(1-c^s) - \frac{RT}{\alpha_B}\ln(1-c) \qquad 21(b)$$

where τ_A and τ_B are surface tension of pure component A and B respectively.

The area of monatomic surface layer for the component i can be calculated by the relation (Butler,1932).

$$\alpha_i = 1.091\ N_0^{1/3}\Omega_i^{2/3} \qquad (22)$$

Where N_0 is Avogadro's number and Ω_i stands for molar volume of the component i, can be calculated from its molar mass and density.

RESULT AND DISCUSSION

The basic inputs for the computation of the thermodynamic properties for binary liquid alloys are energy parameters, i.e. ω and $d\omega/dT$. With the experimental value (Hultgren 1973) of excess free energy of mixing($G_M^{X\,S}$) and heat of mixing (H_M) for equiatomic composition (c =1/2) such energy parameters have been determined using the equations (5) and (7). The best fitted value of the parameters for the alloy Al-Ga at 1023K are found as

$$\omega = 0.0132\text{eV} \quad \text{and} \quad \frac{d\omega}{dT} = -2.208\times10^{-24}\text{JK}^{-1}$$

The estimated energy parameter (ω) is found to small and positive, which suggests that there is higher tendency for like atoms to pair in the alloy which implies a homo-coordination system. We have observed that if energy parameters are supposed to be independent of temperature ($d\omega$ /dT = 0), then S_M and H_M so obtained are in poor agreement with experimental data. This suggests the importance of temperature dependence ordering energy, ω.

The free energy of mixing and entropy of mixing for Al-Ga liquid alloy at 1023K have been computed from equations (6) and (8).The plot of $\frac{G_M}{RT}$ and $\frac{S_M}{R}$ versus cAl are depicted in figure 1. Fig.1 shows that theoretical and
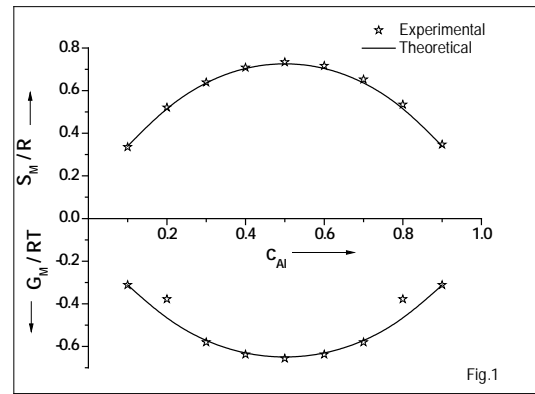

Figure 1: Free energy of mixing (G_M) and entropy of mixing (S_M) Vs concentration of aluminium (c_{Al}) in liquid Al-Ga alloy at 1023K.

experimental values of $\frac{G_M}{RT}$ and $\frac{S_M}{R}$ are in good agreement in all concentrations of aluminium. is $\frac{G_M}{RT}$ minimum but $\frac{S_M}{R}$ maximum at c_{Al} = 0.5, which show that Al-Ga liquid alloy is symmetric about equiatomic concentration. The plot of H_M/RT verses c_{Al} depited in fig.2 also shows that the calculated values of H_M/RT are in good agreement with its experimental values and the alloys is symmetric about equiatomic composition. Positive deviations from Raoultian behaviour was observed in the thermodynamic properties of liquid Al-Ga alloys.

We have used the same value of the energy parameter ω in Eq. 9(a) and 9(b) for the evaluation of chemical activities of the components of the alloy. There is well agreement between theoretical and experimental values of the activities of the components Al and Ga of the alloys (Hultgren et al.).
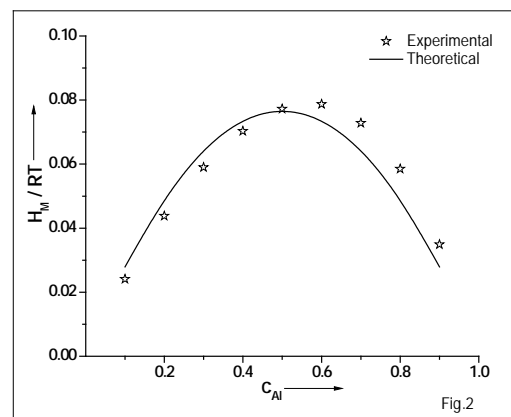

Figure 2: Heat of mixing (H_M) Vs concentration of aluminium (C_{Al}) in liquid Al-Ga alloy at 1023K.

We have used Eq. (12) to compute the S_{cc} (0) for Al-Ga. Figure 4 shows a plot of the calculated and experimental values of S_{cc} (0) along with the ideal values. The calculated values of S_{cc}(0) are in good agreement with the experimental values of S_{cc} (0). The computed Scc(0) nearly attain ideal values, i.e Al-Ga exhibits ideal behaviour for the composition $0 \leq c_{Al} \leq 0.2$ and 0.8

$\leq c_{Al} \leq 1$. But in the region $0.2 < c_{Al} < 0.8$, the computed $S_{cc}(0)$ are greater than ideals values. The result can be used to understand the nature of atomic order in binary liquid alloys. In figure 4, it is seen that $S_{cc}(0) > S_{cc}^{id}(0)$, which shows that liquid alloys Al-Ga at 1023K is of segregating in nature.
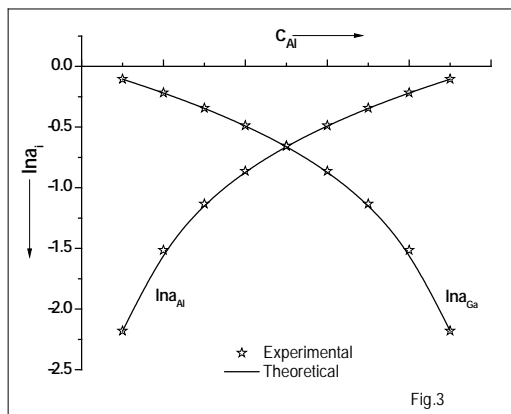

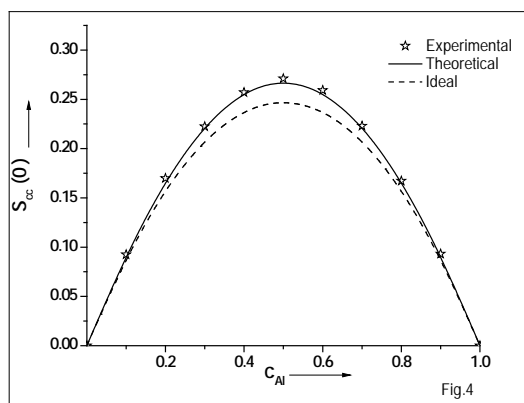Figure 3: Chemical activity (a_i) Vs concentration of aluminium (C_{Al}) in liquid Al-Ga alloy at 1023K.

Figure 4: Concentration fluctuation at long wavelength limit ($S_{cc}(0)$) Vs concentration of aluminium (C_{Al}) in liquid Al-Ga alloy at 1023K.

The knowledge of CSRO parameter α_1 provides an immediate insight into the nature of the local arrangement of atoms in the mixture. Figure 5 shows the plots of α_1 against chemical composition, obtained from Eq.(14) for Al-Ga at 1023K. The positive values of α_1 throughout whole concentration range of Al (fig.5) is the signatures of homo-coordination system in the Al-Ga liquid alloys at 1023K.

The calculated values of $S_{cc}(0)$ are used in Eq. (16) to evaluate the ratio of the mutual and intrinsic-diffusion coefficients, $\frac{D_m}{D_{id}}$. Fig.6 shows plot of $\frac{D_m}{D_{id}}$ against the concentration of aluminium. In that plot the value of $\frac{D_m}{D_{id}}$ is found less than 1 in the entire range of concentration of Al, which is indicative for the phase separation in the mixture. A minimum value of $\frac{D_m}{D_{id}}$ = 0.925 for c_{1n}= 0.5, confirms a weak tendency for segregation, as observed by the $S_{cc}(0)$ and CSRO parameter.
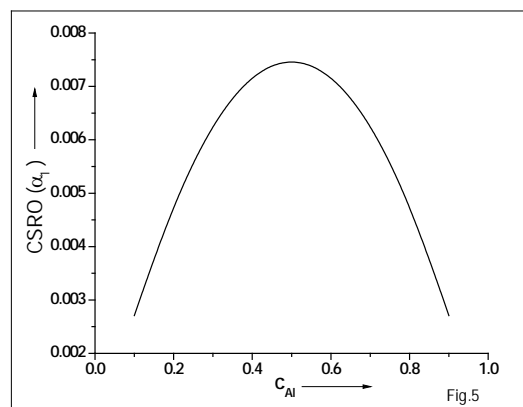

Figure 5: Short range order parameter (α_1) Vs concentration of aluminium (C_{Al}) in liquid Al-Ga alloy at 1023K.
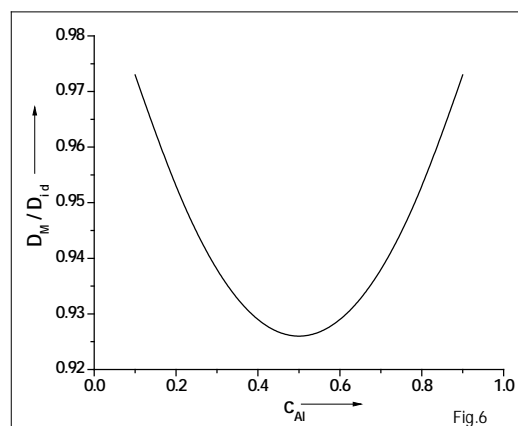

Figure 6: Ratio of chemical and intrinsic diffusion coefficients (D_M/D_{id}) Vs concentration of aluminium (C_{Al}) in liquid Al-Ga alloy at 1023K .

The viscosity of the Al-Ga liquid alloy has been computed numerically from Eq. (15). The plot of η verses bulk concentration of c_{Al} in Al-Ga liquid alloy is shown in fig.7. In figure, small negative deviations from the linear law (Raoult's law) in viscosity isotherms η(c) have been observed for the regular alloy which is the indicative of segregating system.
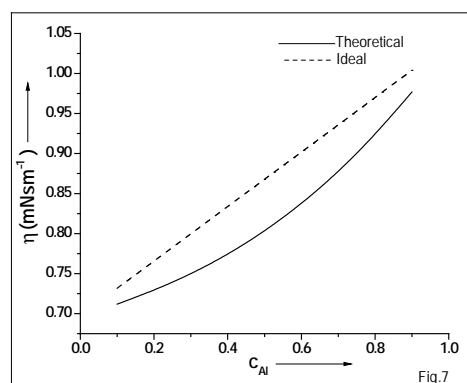

Figure 7:Viscosity (η) Vs concentration of aluminium (c_{Al}) in liquid Al-Ga alloy at 1023K.
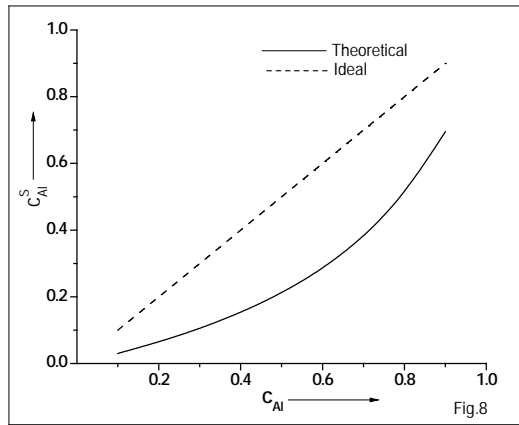
Figure 8: Surface concentration of Al (c^s_{Al}) Vs bulk concentration of aluminium (c_{Al}) in liquid Al-Ga alloy at 1023K.

For the computation of surface concentration and surface tension of the Al-Ga alloy on using Butler's approach, the partial excess free energies of mixing of pure components of the alloys have been taken from the ref.(Hultgren et al,1973).By concurrently solving the equations 21(a) and 21(b), surface concentrations of Al in alloy Al-Ga have been obtained as a function of bulk concentration and then using the obtained values of surface concentrations we computed the surface tension of Al-Ga liquid alloys at temperature 1023K for whole concentration range.
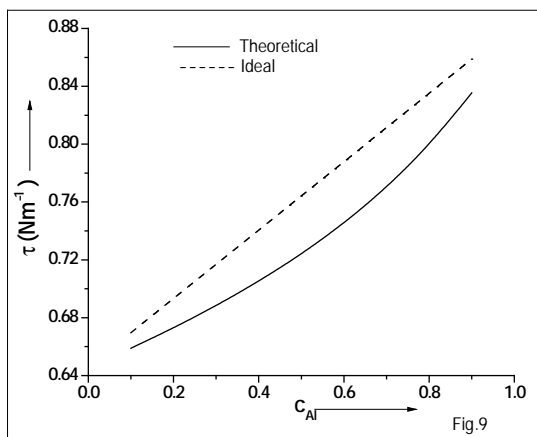

Figure 9: Surface tension (τ) Vs concentration of aluminium(c_{Al}) in liquid Al-Ga alloy at 1023K.

Figures (8) and (9) are respectively the plots of surface concentration and surface tension against bulk concentration of aluminium in liquid Al-Ga alloys at 1023K. It is noticed that surface concentration of aluminium in Al-Ga alloys is found to be larger than concentration from additive rule; it increases with increase of its bulk concentrations [Fig.8]. Theoretical analysis gives that the computed surface tension for Al-Ga alloys at 1023K is less than ideal values at all concentration of aluminium; i.e. there is negative departure of surface tension from ideality. Butler's approach predicts that surface tension of Al-Ga liquid

alloy decreases with increase of bulk concentration of aluminium [Fig.9]. This is an indication that in the alloys there are more atoms of component with bigger atom at the surface. Hence, at the surface of Al-Ga, bigger Ga-atoms segregate at the surface in preference to Al-atoms throughout the entire composition. The segregation of the components may result from the differences surface tension, atom radius and electron configuration between solvent and solute.

CONCLUSIONS

Following conclusions are drawn about liquid Al-Ga alloys at 1023K:

1) Order energy is small, positive and found to temperature dependent.

2) The alloy is of a weakly interacting nature.

3) It is of phase-segregating system.

4) Positive departure of thermodynamic and structural parameters from ideality is observed.

5) Viscosity and surface tension isotherm of the alloy is found to deviate negatively from ideality.

6) The surface of liquid Al-Ga alloys is enormously rich with bigger Ga atoms.

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