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Thermodynamic and structural behaviour of liquid Al-Ga alloys

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ABSTRACT

Quasi-chemical approximation has been used to study the mixing behaviour of liquid aluminium-gallium binary alloys by computing thermodynamic functions, such as free energy of mixing, heat of mixing, entropy of mixing, activity and microscopic functions, such as concentration fluctuation in long wavelength limit ($S_{cc}(0)$), Warren-Cowley short range order parameter (α_1) and ratio of diffusion coefficients of the alloys at 1023 K. The theoretical analysis reveals that the ordering energy is found to be temperature dependent and Al-Ga alloy in molten state is slightly segregating. Copyright © 2013 VBRI press.

Keywords: Binary alloy; quasi-chemical approximation; structural properties; segregating system.

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Introduction

The mixing properties of liquid alloys are important in metallurgical science for understanding process of material preparation of metal alloys. Due to the strong correlations among the particles and their state of disorder, the formulation of exact theory of liquid alloy to understand thermodynamic and structural properties presents a problem of extreme mathematical complexity. It is much more difficult to understand the properties of disordered materials like binary alloys as compared to those of crystals [**1**]. The mixing properties of binary liquid alloys can be attributed to the local ordering of atoms of the constituent species in the alloy. The preference of hetero-pairs or homo-pairs in liquid alloys is also partially understood. To solve these complexities and obtain the thermodynamic properties of mixing of binary liquid alloys, researchers have employed various theoretical models [**1-22**]. In this study, we have used simple statistical theory in the framework of quasi-chemical approximation for regular

alloy [**2**] to understand the thermodynamic and structural properties of Al-Ga liquid alloy at 1023 K.

The observed mixing properties, such as free energy of mixing, heat of mixing and entropy of mixing of this alloy at 1023 K, are symmetrical about equiatomic composition [**23**] and the value of concentration fluctuations in long wavelength limit ($S_{CC}(0)$) calculated from the activity data [**23**] shows that the alloy is segregating in nature even though atomic volume mismatch ($\Omega_{Ga}/\Omega_{Al} = 1.18$) and electronegativity difference (E_{Ga}-E_{Al} = 0.20) are not significantly large. This nature is contradictory to the Hume-Ruthery rule for metal solution. These interesting aspects of Al-Ga liquid alloy led authors for the investigation of its thermodynamic and structural properties.

Aluminium has large negative free energy with strong capacity of formation of its oxide. It, therefore, has thermodynamic ability to split water. The liquid alloys of Al-Ga spontaneously produce hydrogen if mixed with water [**24**]. When Al-component is dissolved in liquid Ga-component just above room temperature the liquid alloy readily reacts with water to form hydrogen. In this process the Ga- component is inert which means it can be recovered and reused [**24,25**]. This technology could be used to generate hydrogen on demand and hence unnecessary storage of hydrogen is not required. In addition aluminium alloys are generally lighter and stiffer and can be considered better construction material than steel in many applications.

Basic formalism of Quasi-chemical approximation is given is section 2. Section 3 deals with the results and discussions and conclusions are outlined in section 4.

Formalism

The quasi-chemical approximation, developed by Singh and Sommer [**4**], is a simple scheme for demixing liquid alloys. It assumes pairing of like atoms at equivalent sites that have short-ranged interaction between nearest neighbours. Such pairing leads to the formation of self-associates in the alloys. Let a liquid binary A-B alloy consist of N_A atoms of element A and N_B atoms of element B which form like atom clusters or self-associates of type μA and υB, where μ and υ are the number of atoms in the clusters of type A and B matrices respectively [**4**]. On the basis of this assumption the expressions for thermodynamic and microscopic functions are derived for binary liquid alloys [**4**].

The free energy of mixing, G_M for binary liquid alloys in quasi-chemical approximation can be obtained using the expression [**4**]

$$G_M = RT\,[c\ln c + (1-c)\ln(1-c) + c\ln(1-\xi) + \ln\Gamma] + c(1-c)\,\Gamma W \quad (1)$$

where, R = universal gas constant, T = the temperature, c = concentration of A-component of the alloy, $\xi = 1 - 1/n$, $\Gamma = 1/(1-c\xi)$, $n = \nu/\mu, \nu \neq \mu$ and W = ordering energy parameter. Here n and W are the parameters to be fitted at a given temperature to estimate the thermodynamic and structural properties of a binary liquid alloy.

In order to obtain the expression for the *activity*, a_i of constituent element in binary liquid alloys we recall the following standard thermodynamic relation which relates activity, a_i to the free energy of mixing, G_M-

$$RT\ln a_i = G_M + (1-c)\frac{\partial G_M}{\partial c} \quad \text{where, i = A, B} \quad (2)$$

Using Eqs. (1) and (2), we get-

$$\ln a_A = \ln[c\Gamma(1-\xi)] + (1-c)\xi\Gamma + (1-c)^2\Gamma^2\frac{W}{RT} \quad (3)$$

and

$$\ln a_B = \ln(c\Gamma) + c(1-\xi)\Gamma(1-n) + nc^2(1-\xi)\Gamma^2\frac{W}{RT} \quad (4)$$

The entropy of mixing, S_M for binary alloys can be obtained using the thermodynamic relation-

$$S_M = -\left(\frac{\partial G_M}{\partial T}\right) \quad (5)$$

which, with use of Eqn. (1) is obtained as-

$$S_M = -R[c\ln c + (1-c)\ln(1-c) + c\ln(1-\xi) + \ln\Gamma] + c(1-c)\,\Gamma\frac{\partial W}{\partial T} \quad (6)$$

Once the free energy of mixing, G_M and entropy of mixing, S_M are obtained, the heat of mixing, H_M can be readily calculated from the standard thermodynamic relation-

$$H_M = G_M + TS_M \quad (7)$$

The microscopic structures such as concentration fluctuations in long wavelength limit ($S_{CC}(0)$) and Warren - Cowley [**21,22**] short-range order parameter (α_1) are useful properties to obtain valuable information about structure of molten alloys. $S_{cc}(0)$ indicates nature of chemical ordering and α_1 represents the degree of ordering in the melt.

The standard relation for concentration fluctuation in long wavelength limit ($S_{CC}(0)$) for binary liquid alloys is given as-

$$S_{cc}(0) = RT\,(\partial^2 G_M/\partial c^2)^{-1}_{T,P,N} \quad (8)$$

Using Eqs. (1) and (8), we get

$$S_{cc}(0) = \frac{c(1-c)}{1 - c(1-c)\,f(n,W)} \quad (9)$$

where

$$f(n,W) = \frac{2n^2(W/RT) - (n-1)^2[c + n(1-c)]}{[c + n(1-c)]^3} \quad (10)$$

The equation for calculation of observed values of $S_{cc}(0)$ is as follows:

$$S_{cc}(0) = \frac{(1-c)\,a_A}{\frac{\partial a_A}{\partial c}} \qquad (11)$$

Warren-Cowley short-range parameter, α_1 can be estimated from the knowledge of $S_{cc}(0)$ using the expression-

$$\alpha_1 = \frac{S-1}{S(z-1)+1}, \qquad S = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \quad \text{where} \quad S_{cc}^{id}(0) = c\,(1-c) \qquad (12)$$

where z represents the number of atoms in the first coordination shell and is called coordination number.
The mixing behaviour of the alloy forming molten metals can also be studied at the microscopic level in terms of the transport properties such as coefficients of diffusion. The $S_{cc}(0)$ and diffusion coefficients can be related using Darken thermodynamic equation for diffusion as follows[**4,26,27**]:

$$\frac{D_M}{D_{id}} = \left[1 - \frac{2W}{RT}\, S_{cc}^{id}(0)\right] = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \qquad (13)$$

where D_M is the chemical or mutual diffusion coefficient and D_{id} the intrinsic diffusion coefficient for an ideal mixture given as,

$$D_M = D_{id}\,\frac{\partial \ln a_A}{\partial c} \qquad (14a)$$

$$\text{with} \quad D_M = c\,D_B + (1-c)\,D_A \qquad (14b)$$

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

Results and discussion

For the computation of the thermodynamic properties for binary liquid alloys on the basis of QCA, the basic inputs are interaction energy parameter, W and ratio of self-associates, n. These fitting parameters have been adjusted in equation (1) for all concentrations. The best fit values of ratio of self associates and interaction energy parameter for the alloy Al-Ga in the molten state at 1023 K are found to be

$n = 0.97$ and $W/RT = +0.15$

The positive value of energy parameter (W/RT) suggests that the alloy is a homo-coordination system, i.e. like atom pairing (Al-Al or Ga–Ga) is preferred. However, the tendency of pairing is very weak since the energy parameter is very small.

The observed values of free energy of mixing of liquid Al-Ga alloy at 1023K is symmetric about equiatomic composition, $c = 0.5$, with a minimum value of -5.576 kJ mol^{-1} [**23**]. The theoretical analysis confirms the symmetric nature of free energy of mixing of this alloy about equiatomic composition with a minimum value of -5.579 kJ mol^{-1}. The theoretical and experimental values of G_M are in excellent agreement (**Fig. 1**). The small negative values of free energy of mixing indicate that the Al-Ga alloy at 1023 K in molten state is weakly interacting system.

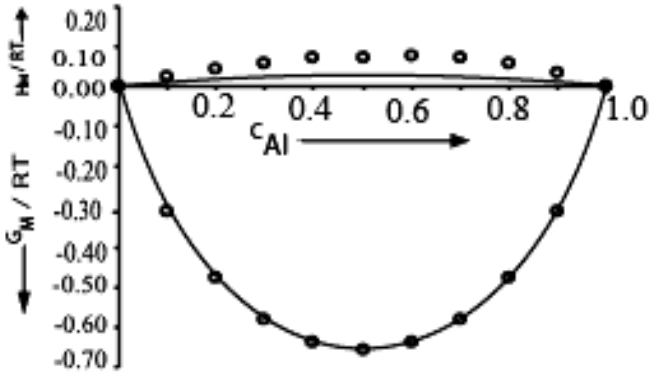

Fig. 1. Free energy of mixing (G_M) and heat of mixing(H_M) Vs concentration of Al (c_{Al}) in liquid Al-Ga alloy at 1023 K; solid lines for theoretical values and circles for experimental values [**29**].

We have observed that if the energy parameters are supposed to be independent of temperature, i.e. if $\frac{\partial W}{\partial T} = 0$, then S_M and H_M so obtained are in very poor agreement with experimental data. This simply suggests the importance of the dependence of interaction energy, W on temperature. The best fit value of the temperature derivative of energy parameter for the Al-Ga alloy at the given temperature is estimated to be $\frac{\partial W}{\partial T} = -0.18R$. With this temperature dependence of energy parameters, we have calculated entropy of mixing, S_M of Al-Ga alloy in molten state from Eqn. (6). The calculated and experimental values of S_M are plotted against the concentration of Al in **fig. 2**. The observed values of S_M [**23**] are symmetrical around equiatomic composition. Our calculated values also show that S_M are symmetrical around $c = 0.5$. The calculated values of S_M are in excellent agreement with the observed values (**Fig. 2**).

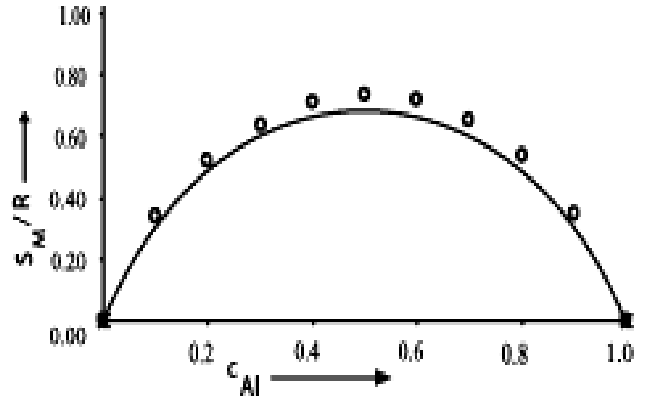

Fig. 2. Entropy of mixing (S_M) Vs concentration of Al (c_{Al}) in liquid Al-Ga alloy at 1023 K; solid lines for theoretical values and circles for experimental values [**29**].

The heat of mixing, H_M of Al-Ga liquid alloy is calculated using free energy of mixing, G_M and entropy of mixing, S_M in equation (7). The calculated values show slight deviation from the experimental values and the deviation is greater toward the Al-rich end of the composition. The difference may be due to the neglect of vibrational and electronic contributions on entropy of mixing. Still the calculated values are symmetrical about $c = 0.5$ as the observed values are and the calculated values for H_M are in reasonable agreement with the observed values [**23**] (**Fig. 1**). Both calculated and observed values are positive for whole range of concentrations of aluminium. This indicates that the system is segregating which is consistent with the ordering energy W.

The activity is one of the important thermodynamic functions which is obtained directly from experiment. Activity is used to calculate the experimental values of $S_{cc}(0)$. The deviation from the ideal behaviour is incorporated into activity. Their magnitudes are assumed to be determined by the interaction among the constituent species of the system which in turn determine the bond energies. Thus measurement of activity within a class of similar systems can be expected to provide at least a basis for correlation of the behaviour which can be used for the extrapolation of behaviour of more complex systems. In order to maintain the consistency in our calculations, we have used the same values of n, W and the temperature derivative of W for the computation of activity. The values of the activities of the component metals calculated using equations (3) and (4) are found in good agreement with the experimental values [**23**] (**Fig. 3**).

The concentration fluctuations in long wavelength limit ($S_{CC}(0)$) can be used to understand the nature of atomic order in the binary liquid alloys. If $S_{cc}(0) < S_{cc}^{id}(0)$, there is ordering and if $S_{cc}(0) > S_{cc}^{id}(0)$, there is a tendency of phase separation. We have found both theoretical and observed values of $S_{cc}(0)$ calculated respectively from equations (9) and (11) greater than ideal values, $S_{cc}^{id}(0)$ at all concentrations (**Fig. 4**). This indicates that self association of atoms (i.e. Al-Al, Ga-Ga) is preferred in molten Al-Ga alloy at 1023K.

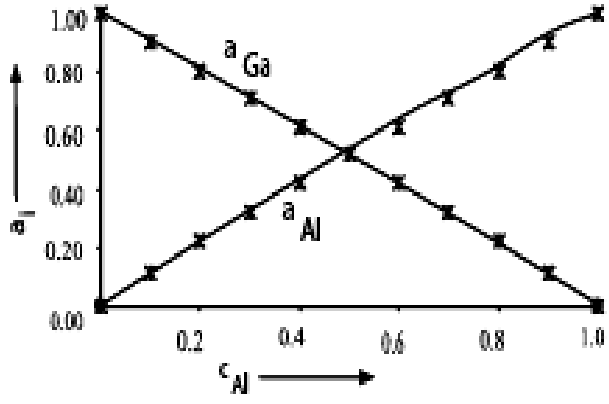

Fig. 3. Chemical activity (a_i) Vs concentration of Al (c_{Al}) in liquid Al-Ga alloy at 1023 K; solid lines for theoretical values and circles for experimental values [**29**].

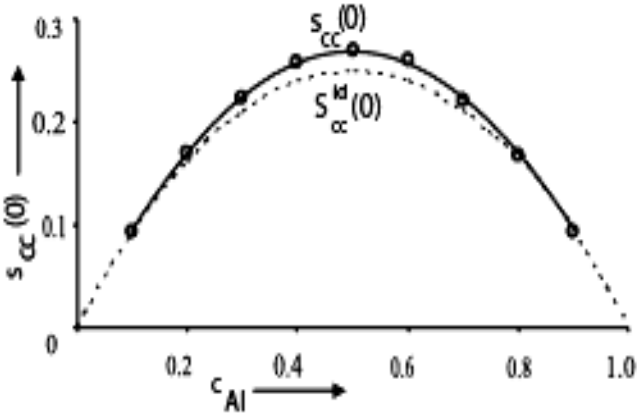

Fig. 4. Concentration fluctuations at long wavelength limit ($S_{CC}(0)$)) Vs concentration of Al (c_{Al}) in liquid Al-Ga alloy at 1023K; solid lines for theoretical values, circles for experimental values [29] and crosses for ideal value.

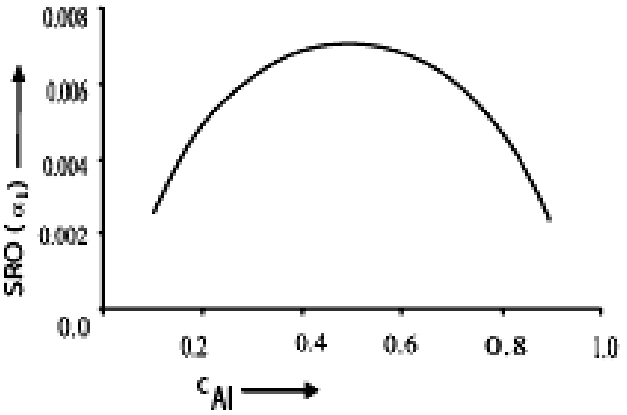

Fig. 5. Short range order parameter (α_1)) Vs concentration of Al (c_{Al}) in liquid Al-Ga alloy at 1023K.

The knowledge of short range order parameter, α_1 provides an immediate insight into the nature of the local arrangements of atoms in the liquid mixture. The normalized values of this parameter provide the strength of the local order of atoms. If α_1 is positive, there is tendency of segregation and if α_1 is negative, there is tendency of ordering. $\alpha_1 = -1$ implies complete ordering of unlike atoms (hetero-pairs); $\alpha_1 = +1$ implies complete segregation (pairing of like atoms or homopairs) leading to the phase separation and $\alpha_1 = 0$ corresponds to a random or ideal mixing of atoms. Thus in order to get better understanding of the local ordering of atoms in the molten alloys, we have calculated α_1 using calculated values of $S_{cc}(0)$ in the equation (12). We have found α_1 small positive for all concentrations which indicates that there is weak tendency of phase separation in the molten Al-Ga alloy at 1023 K (**Fig. 5**). This is in support of the result obtained from the calculation of H_M and $S_{cc}(0)$.

Fig. 4 and **5** show maximum values of $S_{cc}(0)$ and α_1 respectively at 0.269 and 0.0071 at equiatomic composition. Since the deviation in $S_{cc}(0)$ from the ideal value is small and the maximum positive value of α_1 is

also a very small, obviously the liquid Al-Ga alloy at 1023 K is weakly segregating in nature. For the metals in the alloy in liquid phase, the value of coordination number (z) has been taken as 10. We note that varying the value of z does not have any effect on the position of the minima of α_1; the effect is to vary the depth while the overall feature remains unchanged.

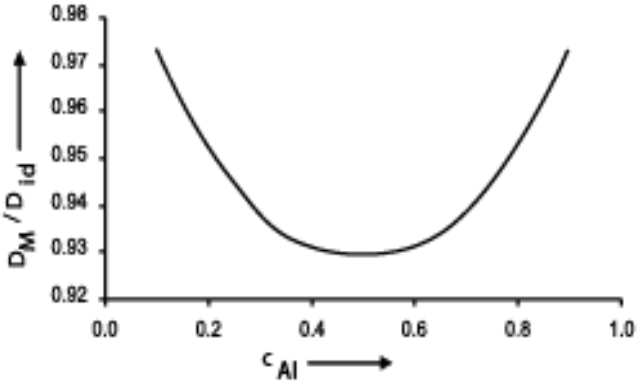

Fig. 6. Ratio of chemical and intrinsic diffusion coefficients (D_M/D_{id}) Vs concentration of Al (c_{Al}) in liquid Al-Ga alloy at 1023K.

The mixing behaviour of binary liquid alloys can also be studied at the microscopic level in terms of transport properties such as chemical diffusion coefficients, viscosity etc. In the present study we have calculated the ratio of mutual diffusion coefficient and intrinsic diffusion coefficient using calculated values of Scc(0) in equations (13). Positive values of this ratio ($D_M/D_{id} < 1$) in the entire range of concentration indicate that the Al-Ga liquid alloy at 1023 K is a weakly segregating system. Since D_M/D_{id} is smaller in intermediate region than in other regions the theoretical calculation indicates that the phase separating tendency of the liquid alloy is maximum at the intermediate composition (**Fig. 6**).

Conclusion

Present theoretical analysis reveals that Al-Ga alloy in the liquid state at 1023 K is weakly interacting system. The alloy consists of weakly bonded like atom clusters or homo-coordinations (i.e. Al-Al, Ga-Ga). The ordering energy is found to be temperature dependent. It is worth-full to mention that the temperature dependence of the ordering energy can be used to study the critical mixing of binary systems.

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