ENTROPY OF MIXING OF NaCd AND AlMg MOLTEN ALLOYS

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Abstract: The complex formation model is used to explain the anomalous behaviour of entropy of mixing of NaCd and AlMg liquid alloys as a function of concentration.The interionic pair potential $\phi_{ij}(r)$ evaluated within the framework of pseudopotential theory which in turn is used to obtain the values of hard-sphere diameter of NaCd and AlMg liquid alloys. The hard-sphere diameter is used to evaluate the concentration dependent anamoly in entropy of mixing which occurs due to preferential ordering of unlike atoms as nearest neighbour on NaCd and AlMg liquid alloys, which could be simultaneously understood with the help of complex formation model. The computed value of Entropy of mixing (S_M) from pseudopotential theory is positive at all concentration range except $0.8 \leq C_{cd} \leq 0.9$in NaCd liquid alloys. The disagreement between theory and experiment might be due to parameterisation of hard- sphere diameter of the complex (σ_3) and ψ_{comp} .

Key Words: Entropy of mixing; Pseudopotential theory; Hard-sphere diameter; Pair-Potential.

1. INTRODUCTION

Various theoretical models[1–6], based on the formation intermetallic compounds, pseudomolecules, complexes in the melt are used to study the energetics of strong interacting binary liquid alloys. Stronger interaction[7] corresponds to greater possibility of compound formation. The first principal theory in the framework of pseudopotential formalism can be used to calculate the pair-potential which subsequently, can be used to study the interionic interaction[8-10], but pseudopotential theory, itself suffers from limitations. For those alloys, whose mixing properties exhibit anomalous behaviour due to strong interaction between the unlike atoms leading to compound formation, pseudopotential theory cannot be applied with confidence[7,8,11]. In view of limitation, the pseudopotential theory requires improvement, so that it could be applied strongly to such alloys.

In this work an attempt has been made for study the entropy of mixing of NaCd and AlMg alloys as a function of concentration on the basis of pseudopotential formalism.

Hoshino and Young[11-13] have used the hard-sphere model to compute the entropy of mixing. The hard -sphere diameter (σ) evaluated from interionic pair potential $\phi_{ij}(r)$ which is evaluated in particular from the band structure energy of pseudopotential theory[7-10]. The concentration dependent thermodynamic properties[14-17] of liquid NaCd and AlMg alloys have been reported interesting features. Thermodynamical [16-17,25] properties were deviated maximally from the ideal values around the concentration close to the configuration Cd_2Na and Al_3Mg_2.

2. COMPLEX FORMATION MODEL FOR ENTROPY OF MIXING

2.1. FORMALISM

The properties of many binary liquid alloys exhibit a pronounced asymmetry as a function of concentration even though the size effect is not large enough to cause the asymmetry. These liquid alloys have the characteristics that in the solid state that they form complexes, at some stoichiometric composition. Therefore, it is tempting to assume that such chemical complexes or pseudomolecules ($\mu A + \nu B \rightleftharpoons A_\mu B_\nu$, A and B are constituent atoms, μ and ν are very small integers) also exists in the liquid phase, close to the melting temperature. The model explains successfully the concentration fluctuation in the long wavelength limit and thermodynamic properties of a number of binary liquid alloys [2, 4, 6, 18-22, 25]

This encourages us to study the entropy of mixing of AlMg and NaCd liquid alloys as a function of concentration.

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A binary liquid alloys containing in all N_A [$=N(1\text{-}C)$] of atoms A and N_B [$=(NC)$] of atoms of B may be assumed to consists of n_m ($=n_3N$) complexes, which also acts as independent scattering centres to the alloy, the total number of scattering points are

$$N_s = n_A + n_B + n_m = nN \tag{1}$$

Where $n=n_1+n_2+n_3$

From the conservation of atoms we have

$n_A + \mu\, n_m = N_A$

$n_B + n_m = N_B$

$n_1 = 1\text{-}C\text{-}n_3$

$n_2 = C\text{-}n_3$

$$n = 1\text{-}(+\text{-}1)n_3 \tag{2}$$

Here C is the concentration of the second species.

The volume in which n_A atoms of A and n_B atoms of B are randomly distributed and can be expressed as;

$$\Omega = \Omega_{\text{alloy}} - n_m V_m \tag{3}$$

Where Ω_{alloy} is the atomic volume of the alloy and V_m is the volume of the complex.

$$V_m = \mu\Omega_1 + v\Omega_2 \tag{4}$$

Where Ω_1 and Ω_2 are the atomic volumes of first and second species of the alloys respectively.

The value of σ_i (hard sphere diameter) as a function of concentration have been determined by minimizing the interionic pair potential ϕ, i.e.

$$\phi(\sigma_1) = \frac{3}{2}K_B T + \varphi_{\min} \tag{5}$$

where $\frac{3}{2}K_B T$ is the mean kinetic energy and $\varphi_{\min}$ is the depth of first minimum in the interionic pair potential.

Using the complex formation model we can express the entropy of mixing forming liquid alloys as[11, 23],

$$S_M = S_{\text{gas}} + S_C + S_n + S_\sigma + S_{\text{comp}} \tag{6}$$

The term S_{gas} is given by:

$$\frac{S_{\text{gas}}}{K_B} = n\left[2.5 + \ln\left\{\Omega s_c\left(\frac{m_1^{x1} m_2^{x2} m_3^{x3} K_B T}{2\Pi h^2}\right)^{\frac{3}{2}}\right\}\right] \tag{7}$$

Here m_1, m_2, m_3 are masses of the first atom, second atom and the complex, K_B is the Boltzman constant and T is the absolute temperature. S_c is the ideal mixing term.

$$\frac{S_c}{K_B} = -n\left(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3\right) \tag{8}$$

Where x_i (i=1, 2, 3) are the concentration fraction of difference scattering centres. The total packing term S_η is given by

$$\frac{S_\eta}{K_B} = -n(r-1)(r+3) \tag{9}$$

With $r = \dfrac{1}{1-\eta}$

η is the packing density defined as

$$\eta = \frac{\Pi}{6\Omega_{alloy}}\left(x_1\sigma_1^{\ 3} + x_2\sigma_2^{\ 3} + x_3\sigma_3^{\ 3}\right) \tag{10}$$

Where σ_1, σ_2 are diameter of the species 1 and 2 and σ_3 is the diameter of the complex.

S_σ arise, due to the difference among the diameters of the free atoms and the complex and is given by

$$\frac{S_\sigma}{K_B} = S_\sigma(1,2) + S_\sigma(1,3) + S_\sigma(2,3) \tag{11}$$

Where

$$\begin{gathered} S\sigma(i, j) = X_i X_j (\sigma_i - \sigma_3)^2 \\ \left\{\left[r(r-1) - \ln r\right]\left(\beta_1^{\ ij} + \beta_2^{\ ij}\right) + 3(r-1)\beta_1^{\ ij}\right\} \end{gathered} \tag{12}$$

$$\beta_1^{\ ij} = \frac{\sigma_i + \sigma_j}{\sigma^3}$$

$$\beta_2^{\ ij} = \sigma_i . \sigma_j \left(x_1\sigma_1^{\ 2} + x_2\sigma_2^{\ 2} + x_3\sigma_3^{\ 2}\right)/\sigma^6$$

$$\sigma^3 = \left(x_1\sigma_1^{\ 3} + x_2\sigma_2^{\ 3} + x_3\sigma_3^{\ 3}\right)$$

S_{comp} is the contribution from the internal degrees of freedom of the complexes which is due to the internal modes of vibration. It is approximated by a sum of contribution from each complex, ψ_{comp} and this may be written as

$$\frac{S_{\text{comp}}}{K_B} = n_3 \Psi_{\text{comp}} \tag{13}$$

In view of expression (6), the entropy of mixing of complex forming liquid alloys can be expressed as

$$\Delta S_M = \Delta S_{\text{gas}} + \Delta S_\eta + S_c + S_\sigma + S_{\text{comp}} \tag{14}$$

Where

$$\Delta S_i = \Delta S_{i,\text{alloys}} - (1-C)S_{i1} - CS_{i2}\left(i = gas, \eta\right) \tag{15}$$

Where S_1 and S_2 are entropies of pure compounds, whose explicit expression can be obtained from above by setting either C=0 or C=1.

3. RESULTS AND DISCUSSION

The entropy of mixing of compound forming alloys NaCd and AlMg is computed using equation (14). The packing density (η) used for this computation has been obtained by using equation (10). The hard-sphere diameters σ_1, σ_2 (1, 2 = constituent atoms used for the computation are taken from Tables 1 and 2). The value of σ_3 (hard sphere diameter for the complex) is fixed by adjusting its value through equation (12) so that a good fit for S_M (experimental) value is obtained. The respective values of σ_3 thus evaluated as 6.56 and 6.51 respectively, for NaCd (T=673K) and AlMg (T=1073K) systems.

ψ_{comp} appearing in equation (13) can be evaluated from the work of Hertz-berg [24]. Due to the complexities involved in the determination, we have treated it as a parameter and fixed it as (21.0 K_B) for NaCd and (27.8 K_B) for AlMg alloys.

Table 1: Volume,diameter and hard-sphere diameter for NaCd alloys at 673 K.

C_{Cd}	Volume	σ_{Cd}	σ_{Na}
0.0	300.616	-	6.130
0.1	274.817	5.085	6.145
0.2	252.384	5.013	6.157
0.3	232.192	5.124	6.164
0.4	214.245	5.147	6.167
0.5	197.420	5.168	6.166
0.6	182.838	5.186	6.162
0.7	170.799	5.200	6.155
0.8	162.650	5.210	6.149
0.9	158.160	5.216	6.143
1.0	158.160	5.219	-

*Hoshino *et. al.* (1982), volume at 673K.

Table 2: Volume,diameter and hard-sphere diameter for AlMg alloys at 1000 K.

C_{Al}	Volume	σ_{Al}	σ_{Mg}
0.0	173.00	-	5.613
0.09	167.25	5.303	5.617
0.32	154.22	5.321	5.613
0.425	148.84	5.328	5.610
0.625	140.64	5.338	5.604
0.75	136.20	5.343	5.601
1.0	128.00	5.353	-

* Pelzel *et. al.* (1940), volume at 1000K.

Table 3

Alloy	Temp	$C_{Cd/Al}$	Computed	Expt.
NaCd	673K	0.1	0.243	0.244
		0.2	0.376	0.366
		0.3	0.400	0.359
		0.4	0.338	0.321
		0.5	0.136	0.239
		0.6	0.046	0.143
		0.7	0.270	0.053
		0.8	0.840	-0.010
		0.9	0.670	-0.023
AlMg	1073K	0.09	0.274	0.270
		0.32	0.590	0.525
		0.425	0.519	0.575
		0.625	0.585	0.585
		0.75	0.789	0.530

* Hultgreen *et. al.* 1973

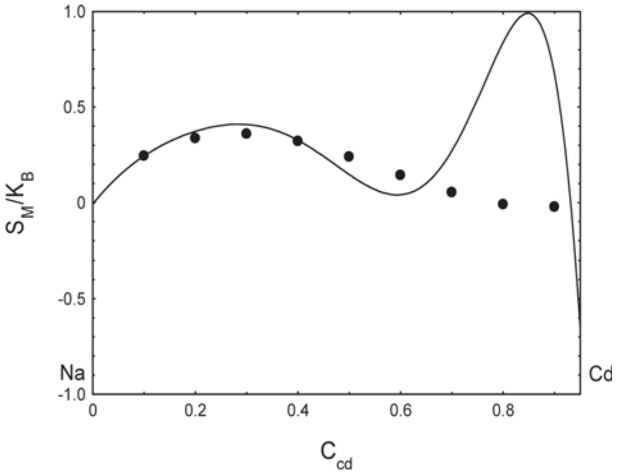

Fig.1: S_M/K_B vs C_{cd} for NaCd liquid alloys at 673K (solid lines): theory; (closed circles): experiment (Hultgren *et. al.* 1973).

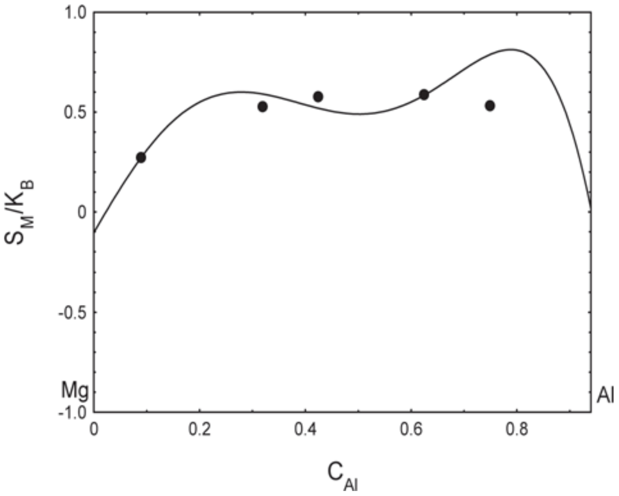

Fig.2: S_M/K_B vs C_{Al} for AlMg liquid alloys at 1073K (solid lines): theory; (closed circles): experiment (Hultgren *et. al.* 1973).

The computed and experimental (Hultgreen *et. al.* 1973) values of S_M for NaCd and AlMg systems are tabulated in Table 3.

The S_M vs C_{Cd} curve for NaCd alloys, (Fig.1) shows good agreement between the computed and experimental values in the concentration range $0.1 \le C_{cd} \le 0.6$, beyond this concentration range a distinct deviation in magnitude of S_M is observed. The theoretical values are all positive, where as the experimental values (Hultgreen *et. al.* 1973) are slightly negative in the concentration range $0.8 \le C_{cd} \le 0.9$.

As for AlMg alloys, computed values agree well with the experimental as shown in (Fig 2). S_M has been found positive at all concentrations.

The disagreement between computed and the experiment might be due to parameterisation of σ_3 and ψ_{comp}.

S_{comp} which is used in equation (13), is the contribution from the internal degrees of freedom of the complexes, which is due to the internal modes of vibration. It is approximated by a sum of contribution from each complexes, S_{comp} is used in equation (14), to get the entropy of mixing value, where ψ_{comp} value is used as a parameter, which may not have explained the internal modes of vibration of the complexes exactly. So, in our work, we have concluded this as a major cause of deviation in case of NaCd alloys at higher concentration. Attempts are being made to improve our theory to give better results.

4. CONCLUSION

Our theoretical study of Na-Cd /Al-Mg alloys, which assumes the existence of Cd_2 Na and Al_3 Mg_2 compound in the melt, explain successfully the concentration dependent asymmetry in the entropy of mixing.

The computed values of S_M/K_B are positive at all concentrations, showing the atomic order. There are reasonable agreement between computed and experimental values in the concentration range of $0.1<C_{cd}<0.6$, beyond this range a distinct deviation in magnitude of S_M/K_B is observed, for NaCd liquid alloy. For AlMg liquid alloys, computed values agree well with experimental values.

The deviation in S_M/K_B values observed might be happening due to parameterization of σ_3 and ψ_{comp}, however attempts are being made to improve the pseudopotential theory so that it could be applied to strong interacting binary system.

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