

Microscopic Structure of NaCd Compound Forming Binary Molten Alloys

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Received March 14th, 2011; revised April 15th, 2011; accepted May 5th, 2011.

ABSTRACT

A simple statistical mechanical theory based on compound formation model (compound $A_\mu B_\nu$ formed by the preferential arrangement of A and B constituent atoms of the alloy AB, $\mu A + \nu B \rightleftharpoons A_\mu B_\nu$) has been used to investigate the phenomena of compound formation in NaCd liquid alloys through the study of concentration fluctuation in the long wave-length region [$S_{CC}(0)$] and chemical short range order parameter (α_1). The study explains the observed asymmetry successfully and suggest the existence of Cd_2Na complex in the melt. The tendency of compound has been found to be weak. A tendency of inversion from segregation to order although very small, has been observed, in NaCd liquid alloys.

Keywords: A Simple Statistical Mechanical Theory, Compound Formation Model, Concentration Fluctuation in the Long Wave Length Region [$S_{CC}(0)$] and Chemical Short Range Order Parameter (α_1)

1. Introduction

Although the value of excess free energy of mixing G_M^{XS} for NaCd liquid alloys is small (-4.49 KJ at $C_{cd} = 0.66$), still it shows asymmetry around equiatomic composition. This interesting aspect led the authors to undertake a theoretical investigation of NaCd liquid alloys. Theoreticians have worked with various theoretical models [1-10], to understand the alloying behavior of compound forming binary molten alloys. All the theoretical model led to the fact that interatomic interaction plays an important role in compound formation. Due to the presence of strong interatomic interaction, these alloys form intermetallic compounds at one or more stoichiometric composition, which is also manifested in their phase diagram.

The formation of compound in solid state led many theoreticians to believe in the existence of chemical complexes, pseudomolecules and privileged group of atoms near the melting temperature in binary liquid alloys.

Many theoretical models based on the above assumptions have been used to investigate the alloying behavior of such type of binary molten alloys. The microscopic properties such as [$S_{CC}(0)$, α_1] show maximum deviation from ideal behavior around compound forming concentration and α_1 has large negative values indicating chemical order essential for compound formation. The phase

diagram of NaCd alloy shows the existence of Cd_2Na compound in the solid state.

Hence, in the present investigation, a simple theoretical model [2,7-11] of compound formation has been used to investigate the asymmetry in the property of mixing [$S_{CC}(o)$, α_1] of Cd_2Na compound forming liquid alloys.

2. Theoretical Consideration

Let the binary solution contains in all $N_A = NC$ and $N_B = N(1 - C)$ gm moles of A and B atoms, respectively, C being the atomic fraction of A atoms. Following Bhatia and Hargroven [1] and Bhatia *et al.* [3], only one type of complex $A_\mu B_\nu$ (μ and ν are small integers) is assumed to be formed. If, in the solution n_1 g mole A atoms and n_2 g mole of B atoms and n_3 g mole of $A_\mu B_\nu$ are formed, then from the law of conservation of atoms,

$$\begin{aligned}n_1 &= NC - \mu n_3 \\n_2 &= N(1 - C) - \nu n_3 \\n &= n_1 + n_2 + n_3 = N - (\mu + \nu - 1)n_3\end{aligned}\quad (1)$$

where n is the total number of atoms in the case of compound formation. Under the frame work of above model, the free energy of mixing G_M can be expressed as

$$G_M = -n_3 g + G' \quad (2)$$

where $(-n_3 g)$ is lowering of free energy due to the forma-

tion of the complex and “ g ” is the free energy of mixing of ternary mixture of fixed n_1 , n_2 and n_3 whose constituents A , B and $A_\mu B_\nu$ are supposed to interact weakly with one another. Flory [12] gave an expression of G' taking into account the difference of size between the unassociated species given as

$$G' = RT \left[\sum_{i=1}^3 n_i \ln(n_i/N) + n_3 \ln[(\mu + \nu)n_3/N] \right] + \sum \sum \left(\frac{n_i n_j}{N} \right) \frac{V_{ij}}{RT} \quad (3)$$

where $V_{ij}(i, j = 1, 2, 3)$ are the interaction energies through which the left over A atom, B atom and the complex $A_\mu B_\nu$ interact with one another. The energies V_{ij} are independent of concentration but may depend upon temperature and pressure. It is convenient to write the expression for G_M from Equations (2) and (3):

$$G_M = -n_3 g + RT \left[\sum_{i=1}^3 n_i \ln(n_i/N) + n_3 \ln[(\mu + \nu)n_3/N] \right] + \sum \sum \left(\frac{n_i n_j}{N} \right) \frac{V_{ij}}{RT} \quad (4)$$

The assignment of the value n_3 for the evaluation of G_M , through Equation (4) is the main problem which can be solved by using equilibrium relation given as

$$\left(\frac{\partial G_M}{\partial n_3} \right)_{T,P,n,C} = 0 \quad (5)$$

Equations (4) and (5) give

$$n_1^\mu n_2^\nu = n_3 N^{\mu+\nu-1} (\mu + \nu) \exp[-(\mu + \nu - 1) - g/RT + Z] \quad (6)$$

where

$$Z = (NRT)^{-1} \left[(n_1 - \mu n_3) V_{13} + (n_2 - \nu n_3) V_{23} - (\mu n_2 + \nu n_1) V_{12} \right] \quad (7)$$

Once the expression for G_M obtained, other thermodynamic and microscopic functions, which are related to G_M through standard thermodynamic relation follows readily as,

$$H_M = G_M - T \left(\frac{\partial G_M}{\partial T} \right)_{T,P,N} \quad (8a)$$

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

$$S_{CC}(0) = NRT \left(\partial^2 G_M / \partial C^2 \right) = (1-C) a_A (\partial a_A / \partial C)_{T,P,N}^{-1} \quad (8c)$$

$$S_{CC}(0) = NRT \left(\partial^2 G_M / \partial C^2 \right) = C \cdot a_B (\partial a_B / \partial (1-C))_{T,P,N}^{-1} \quad (8d)$$

where a_A , a_B are the activities of A and B components respectively. When Equation (4) is used in Equations (8c) and (8d), the expression for $S_{CC}(0)$ is obtained as

$$S_{CC}(0) = \left[N \sum_{i=1}^3 \left(\frac{n'_i}{n_i} \right)^2 + \frac{2}{N^2 RT} \sum \sum n'_i n'_j v_{ij} \right]^{-1} \quad (9)$$

The prime denotes differentiation with respect to concentration *i.e.*

$$\begin{aligned} n'_1 &= 1 - \mu n'_3 \\ n'_2 &= 1 - \nu n'_3 \end{aligned} \quad (10)$$

Differentiation of Equation (6) gives n'_3

The determination of partial structure factor at $q = 0$, *i.e.* $S_{CC}(0)$ poses much more difficult experimental problem and has never been accomplished successfully. Till now $S_{CC}(0)$ can not be evaluated experimentally by diffraction experiment. It can be determined experimentally from the measured activity data following two equalities of Equation (8d). This is usually considered as experimental data.

The chemical short range order parameter (α_1) quantifies the degree of order. It provides the immediate insight into local arrangement of atoms in the alloy. Preference for unlike atoms pairing or heterocoordination is indicated by $\alpha_1 < 1$, whereas like atoms pairing or self coordination is indicated by $\alpha_1 > 1$, $\alpha_1 = 0$ indicates complete disorder of the atom in the alloys.

From probability approach one can show the limiting range of α_1 easily as

$$\begin{aligned} -\frac{c}{(1-c)} &\leq \alpha_1 \leq 1, c \leq 1/2 \\ -\frac{(1-c)}{c} &\leq \alpha_1 \leq 1, c \geq 1/2 \end{aligned} \quad (11)$$

The minimum possible value of $\alpha_1^{\max} = -1$, gives complete order, whereas $\alpha_1^{\max} = +1$, gives complete segregation of atoms in the alloy.

The experimental data of α_1 is also very difficult because it requires the knowledge of $S_{CC}(q)$ and $S_{NN}(q)$ which are concentration-concentration structure factor and number - number structure factor, respectively. However, in practice it is difficult to determine $S_{NN}(q)$ and $S_{CC}(q)$ for all kinds of binary alloys.

The theoretical relation between α_1 and $S_{CC}(0)$ for the first neighbour shell exists as

$$\alpha_1 = \frac{S_1}{[S_{CC}(0)Z - S_1]} \quad (12)$$

Here Z = coordination number, whose value is taken as 10 and $S_1 = S_{CC}(0) - S_{CC}(0, id)$

$$[S_{CC}(0, id) = C(1 - C)] \text{ is the ideal value for } S_{CC}(0) \quad (13)$$

3. Results and Discussion

3.1. Concentration Fluctuation in the Long Wavelength Limit and CSRO (α_1)

Equations (9) and (12) have been used to compute the value of $S_{CC}(0)$ and α_1 , respectively. The basic inputs for the calculation are n_3g and V_{ij} . Equilibrium relation (6) which involves g and V_{ij} are used to calculate n_3 , the method suggested by Bhatia and Hargrove [1] and Bhatia *et al.* [3], which used to obtain the starting value of g and V_{ij} . The value of μ and ν , usually selected from the compositional dependence of physical properties or from the phase diagram, are taken for Cd + Na system, $\mu = 2$, $\nu = 1$. As discussed earlier, the tendency of compound formation is weak in CdNa system, the value of g should be small. Therefore for the starting value one can take $g \approx -(\mu + \nu)G_M$.

The values of g and V_{ij} are adjusted to obtain the concentration dependence of G_M through Equations (4) and (6). The above process repeated until a good fit for G_M or G_M^{XS} is obtained. The value of interaction energy parameters are chosen as

$$\left(\frac{g}{RT} = 1.5, \frac{V_{12}}{RT} = 3.0, \frac{V_{13}}{RT} = 0.9, \frac{V_{23}}{RT} = 1.7 \right) \quad (14)$$

The above set of energy parameters are utilized in Equation (6) to obtain n_3 as a function of concentration. The quantities n_1 and n_2 can be obtained by substitution of n_3 in Equation (1). The computed and experimental values are given in **Table 1** and which are plotted in **Figures 1 and 2** as a function of concentration.

No distinct minimum is observed around compound forming concentration $C_{cd} = 0.66$, but the maximum deviation of $S_{CC}(0)$ from $S_{CC}(id, 0)$, $[S_{CC}(id, 0) - S_{CC}(0)]$ is sufficient to indicate the presence of Cd_2Na complex in NaCd liquid alloy at $C_{cd} = 0.66$ which is compound forming concentration $\left(C_c = \frac{\mu}{\mu + \nu} \right)$.

$S_{CC}(0)$ is greater than $S_{CC}(id, 0)$ in the concentration range $0 < C_{cd} < 0.58$, which indicates the presence of self coordination leading to segregation, being maximum around $C_{cd} = 0.8$. So an inversion from segregation to order is exhibited in NaCd liquid alloys around $C_{cd} = 0.58$.

For the computation of α_1 , Equation (12) is used, where the value of Z is taken equal to 10. For want of experimental values α_1 could not be compared. In order

to quantify the degree of heterocoordination α_1 versus C_{cd} plotted in **Figure 2**. The positive value of α_1 in the concentration range $0 < C_{cd} < 0.58$ indicates segregation or like atoms pairing (Na-Na, Cd-Cd) as nearest neighbour. The negative value of α_1 beyond this range indicates existence of atomic order in the melt. The minimum value of α_1 (-0.176) has been found near compound forming concentration $C_{cd} = 0.66$, which is very low indicating a weak order. The asymmetry in α_1 is distinctly visible in **Figure 2**.

4. Conclusions

The theoretical model presented by authors, which assumes the existence of Cd_2Na compound in NaCd molten alloys explain the concentration dependence asymmetry of mixing properties satisfactorily, computed result show that the tendency of unlike atom pairing (Na-Cd) depends very much on concentration, maximum deviation

Table 1. Concentration fluctuation at the long wavelength limit $S_{CC}(0)$ and chemical short range order parameter (α_1) of NaCd liquid alloys at 673 K.

C_{cd}	$S_{CC}(0)$ Theory	Expt.*	$S_{CC}(id, 0)$	α_1 Theory
0.1	0.210	0.170	0.09	0.060
0.2	0.409	0.366	0.16	0.064
0.3	0.512	0.586	0.21	0.060
0.4	0.470	0.516	0.24	0.048
0.5	0.332	0.308	0.25	0.024
0.6	0.211	0.171	0.24	-0.021
0.7	0.101	0.103	0.21	-0.099
0.8	0.048	0.064	0.16	-0.176
0.9	0.037	0.035	0.09	-0.110

*Hultgren *et al.* [6].

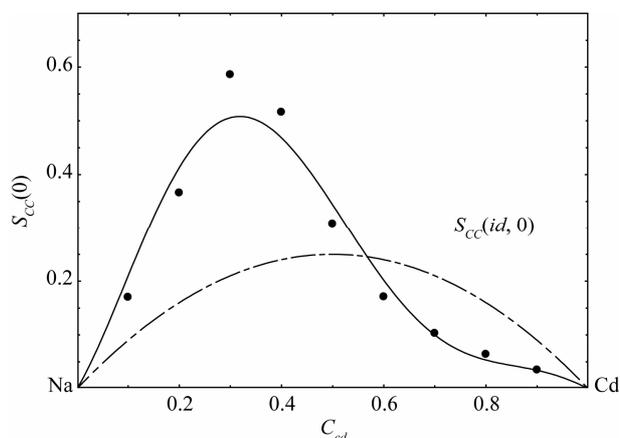


Figure 1. $S_{cc}(0)$ vs C_{cd} for NaCd liquid alloys at 673 K (Solid lines): theory; (Closed circle): experiment.

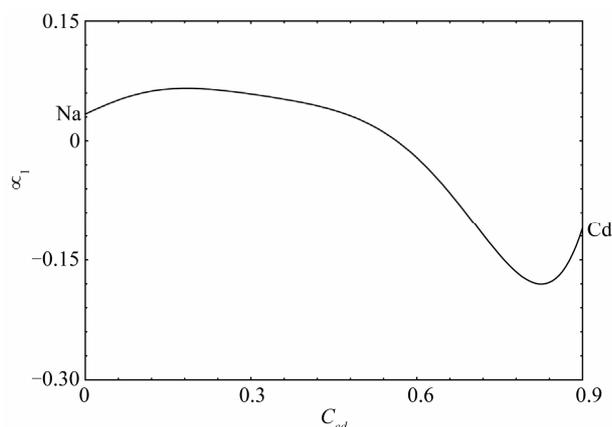


Figure 2. α_1 vs C_{cd} for NaCd liquid alloys at 673 K (Solid lines).

is observed around $C_{cd} = 0.66$, which is compound forming concentration, indicates existence of $Cd_2 Na$ complex in the melt.

The low negative value of α_1 is sufficient to indicate the tendency of compound formation is very weak. An inversion from segregation to order is also clearly visible in NaCd liquid alloys.

5. Acknowledgements

The authors are grateful to Prof. R. N. Singh, presently at the department of Physics, Sultan Quaboos University, Muscat, OMAN for his valuable suggestions and discussions.

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