Thermodynamic Study of Homo-pairs in Molten Cd-Me, (Me=Ga,In) Binary Systems

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Abstract

The associative tendency between like atoms in molten Cd-Ga and Cd-In alloy systems has been studied by using the Quasi-Chemical Approximation Model (QCAM). The concentration dependence of the microscopic functions (the concentrationconcentration fluctuations in the long-wavelength limits, $S_{cc}(0)$, the chemical shortrange order (CSRO) parameter α_1 as well as the chemical diffusion) and the mixing properties as the free energy of mixing, G_M , enthalpy of mixing and entropy of mixing of the two molten alloys have been determined. Thermodynamic properties of both systems deviate positively from Raoult's law, while the systems are characterized by positive interaction energy. The role of atomic size ratio on the alloying properties was discussed.

Keywords: Homo-pairs; Interchange energy; Enthalpy; Entropy; Cd-Ga; Cd-In

1.0 Introduction

The development of improved high strength and high conductivity metal alloys as promising functional materials is a vital activity at the leading edge of science and technology [1,2]. From this basic point of view, the study of thermodynamic properties of binary molten alloys has drawn the attentions of physicists, chemists and metallurgists for sometime, first of all in connection with their use in modern technology, especially in automotive industry as die casting alloys [1,3]. These materials offer unrivalled combination of properties and reliability at a cost which is affordable. They are also versatile because subtle changes in their microstructure by introducing small amounts of various elements, such as cadmium can cause dramatic variations in their properties.

Researchers over the years have used either the quasi-chemical approximation model [4] or any of the other numerous available models [5] to explain the concentration dependent thermodynamic properties of binary molten alloys. However, in the model formulations, the deviation of the properties of an alloy from the ideal mixing behaviour is discussed in terms of the interatomic interactions and related energies of the bonds between the constituent species A and B atoms of a binary alloy. The information on the energetic and the structure of melts as well as the ways how they are coupled are important prerequisites to understanding the mixing behaviour in binary liquid alloys.

In this light, it is interesting to note that a major criteria for choosing a particular thermodynamic alloy to work on is, how far does the liquid alloys thermodynamic properties deviate from the ideal mixture behaviour. Based on the mixing behaviour of the constituent atoms, all liquid binary mixtures can be classified into two main groups: short-range ordered or segregating (demixing). In terms of energetic and structure, the first group is characterized by a strong interactive tendency between unlike atoms and by the formation of hetero-paired A-B pairs of atoms [2-11]; on the other hand, the second one indicates that the attractive force between like atoms is much greater than between unlike atoms, and the formation of homopaired A-A or B-B pairs takes place [11-14].

The Cd-Ga and Cd-In systems are characterized by positive interaction energy, suggesting the probable formation of two-phase structures, as shown by their phase diagram [15]. The symmetric behaviour noticed in the mixing properties for Cd-Ga and Cd-In systems at the equiatomic composition is a result of weak exothermic effects revealed by the preliminary investigation of the Hume-Rothery empirical factors such as size ratio values, ($V_{Ga}/V_{Cd} = 1.101$) and ($V_{In}/V_{Cd} = 1.212$) [16] and electronegativity difference ($E_{Ga}-E_{Cd} = 0.12$) and ($E_{In}-E_{Cd} = 0.09$) [17], indicating values that are characteristic for segregating alloys [13]. In addition, both the activities and the enthalpy of mixing of Cd-Ga and Cd-In molten alloys deviate positively from the ideal values, and thus the two systems belong to the class of liquid alloys that exhibit a tendency towards homo-coordination.

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The motivations to investigate these two molten alloys are borne out of emerging facts from recent studies [18,19] which indicate that addition of a small amount of Cd into the Al-Cu alloy could significantly increase the nucleation rate of θ' phase of the alloy, thus resulting in finer structure and improved the aging strengthening, in addition to the availability of the required experimental data for the model calculations. Also, the effect of Cd on the aging process of quaternary Al-Cu-Mg-Si system as reported by Li et al [19] showed that the strength after aging of Al-Cu-Mg-Si system is increased by about 20% with 0.27% Cd (mass fraction) added. Moreover, Cadmium is a highly reactive element and it is difficult to conduct diffraction experiment on it. Therefore a theoretical investigation giving structural information on a system of Cd is highly desirable to complement experiment. Here, we present a study of the associative tendency between the like atoms (homopairs) in Cd-Ga and Cd-In molten alloys via the quasi chemical approximation model (QCAM), which is helpful to comprehend the interaction between different elements and promote the improvement of existing Cd-based materials as well as for the design of new materials with superior properties by extracting additional information on the peculiarities of effect of different amounts of cadmium on the structure of the alloys studied. Hence, a number of thermodynamic quantities such as the concentration-concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, the Warren-Cowley chemical short-range order (CSRO) parameter, (α_1), the chemical diffusion (D), the thermodynamic activity (a), and other mixing properties as the concentration dependence of the free energy of mixing (G_M), enthalpy of mixing and entropy of mixing were investigated. Theoretical basis of the QCAM is given in section 2, section 3 deals with the numerical results and discussion. And conclusion is provided in section 4.

2.0 Theoretical Concepts

The grand partition function Ξ of a binary molten alloy A-B consisting of $N_A = Nc$ and $N_B = N(1-c)$ atoms of elements A and B respectively, where the total number of atoms, N, is equal to $N_A + N_B$, can be expressed as:

$$\Xi = \sum_{E} q_{A}^{N_{A}}(T) q_{B}^{N_{B}}(T) \exp[\mu_{A} N_{A} - \mu_{B} N_{B} - E] / k_{B} T$$
(1)

Where $q_i^N(T)$ and μ_i are atomic partition function and chemical potential of i^{th} components (i = A, B), k_B is Boltzmann's constant, T is the absolute temperature and E is the configurational energy of the alloy.

After doing some algebra [10], the solution of equation (1) is given as the ratio of the activity coefficient of alloy components, γ , ($\gamma = \gamma_A/\gamma_B$):

$$\ln \gamma = \frac{Z(1-c)}{2c} \cdot \frac{(\beta + 2c - 1)}{(\beta - 2c + 1)}$$
(2)

with

$$\beta = \{1 + 4c(1 - c)(\eta^2 - 1)\}^{1/2}$$
(3)

where

$$\eta^2 = \exp\left(\frac{2\omega}{zk_BT}\right) \tag{4}$$

and the interchange or ordered energy, ω is expressed as

$$\omega = Z[\Delta \varepsilon_{AB} - \frac{1}{2}(\Delta \varepsilon_{AA} + \Delta \varepsilon_{BB})]$$
⁽⁵⁾

 $\Delta \epsilon_{AB}$, $\Delta \epsilon_{AA}$, $\Delta \epsilon_{BB}$ are the interaction parameters and $\Delta \epsilon_{ij}$ is the change in the energy of the *ij* bond in the complex $A_{\mu}B_{\nu}$, Z is the coordination number, c is the concentration of atom A and R is the universal gas constant.

The Gibbs free energy of mixing G_M is obtained from equation (2) via standard thermodynamic relations [8] as:

$$G_{M} = RT \{ c \ln c + c(1-c) \ln(1-c) + c \ln \gamma_{A} + (1-c) \ln \gamma_{B} \}$$
(6)

$$\gamma_{A} = \left\{ \frac{\beta - 1 + 2c}{c(1 + \beta)} \right\}^{z/2} \qquad ; \qquad \qquad \gamma_{B} = \left\{ \frac{\beta + 1 - 2c}{(1 - c)(1 + \beta)} \right\}^{z/2} \tag{7}$$

where γ_A and γ_B are activity coefficients of atoms A and B, respectively. And, activity is given by

$$a_i = c\gamma_i$$
; $(i = A, B)$ (8)

The concentration-concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, has emerged as one of the powerful microscopic functions for visualizing the mixing behaviour of liquid alloys in terms of compound formation and phase Journal of the Nigerian Association of Mathematical Physics Volume 26 (March, 2014), 187 – 194

segregation [8]. The $S_{cc}(0)$ can be expressed in terms of G_M or activities a_i (i = A, B), as:

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial c_A^2}\right)_{T,P,N}^{-1} = c_A c_B \left(\frac{\partial a_B}{\partial (1-c_A)}\right)_{T,P,N}^{-1}$$
(9)

For ideal mixing the energy parameters, ω , given in equation (5) is equal to zero, and equation (9) becomes:

$$S_{\alpha}^{id}(0) = c_A c_B \tag{10}$$

Substituting eqn.(6) for G_M into eqn.(9), one obtains

$$S_{cc}(0) = \frac{c(1-c)}{1 + \frac{z}{2} \left(\frac{1}{\beta} - 1\right)}$$
(11)

Equation (9) is usually utilized to obtain the experimental values of $S_{cc}(0)$ from the measured free energy of mixing data or activity data [12]. The alloying behaviour of molten binary alloys can be inferred from the deviation of $S_{cc}(0)$ from $S^{id}_{cc}(0)$. The presence of chemical order is indicated by $S_{cc}(0) < S^{id}_{cc}(0)$; on the contrary, if $S_{cc}(0) > S^{id}_{cc}(0)$, the segregation and demixing in liquid alloy take place.

The Warren-Cowley short-range order parameter, α_1 [11,12] is computed to quantify the degree of order in the molten alloys. This parameter α_1 is expressed in term of β -function (equation (3), as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{12}$$

Another formalism that relates chemical diffusion and $S_{cc}(0)$ through the basic thermodynamic relations [12] as well as Darken's thermodynamic equation for diffusion was also computed to quantify the mixing behaviour of two molten metals forming alloys at the microscopic scale, in the form:

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{ia}(0)}{S_{cc}(0)}$$
(13)

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

$$D_{id} = c_A D_A + c_B D_B \tag{14}$$

with D_A and D_B being the self-diffusion coefficient of pure components A and B, respectively. The enthalpy of mixing, H_M within the quasi-chemical model (QCM) can be obtained

from the standard thermodynamic relation [13]

$$H_{M} = G_{M} - T \left(\frac{\partial G_{M}}{\partial T}\right)_{p}$$
(15)

From the expression for G_M in equation (6), we obtain

$$H_{M} = \frac{8RTc^{2}(1-c)^{2} \exp\left(\frac{2\omega}{zk_{B}T}\right)}{(\beta-1+2c)(1+\beta)(\beta+1-2c)} \left(\frac{1}{k_{B}}\frac{d\omega}{dT} - \frac{\omega}{T}\right)$$
(16)

and the entropy of mixing,

$$S_M = \frac{H_M - G_M}{T} \tag{17}$$

3.0 Result and Discussion

The first important task carried out was the assessment of the phase diagrams of Cd-Ga and Cd-In molten alloys and preliminary investigation of their Hume-Rothery empirical factors such as size ratio values and electronegativity differences. Thereafter, one then proceeds using Eqn. (6) to determine the optimal values of the interaction energy parameters that best reproduced to a reasonable extent the experimentally measured free energy of mixing, G_M taken from [15]. Table 1 shows the values of the fitted interaction parameters for the molten Cd-Ga and Cd-In alloys. Keeping these fitted parameters constant, a *Journal of the Nigerian Association of Mathematical Physics Volume 26 (March, 2014), 187 – 194*

number of thermodynamic properties such as G_M , $S_{cc}(0)$, a_i , α_1 , D, H_M and S_M have been computed thus, forming the basis to understand the energetic of Cd-Ga and Cd-In molten alloys.

The computed and experimental values of G_M/RT as a function of composition computed via Eqn. (6) are given in Fig. 1 for the two alloys. It can be seen from Fig. 1 that the values of G_M are negative at all concentrations and the curves for both Cd-Ga and Cd-In systems exhibit minimum G_M values at -0.235RT and -0.539RT, respectively. Thus suggesting that the two alloys are neither such a strongly interacting systems as Fe-Pt and Ni-Pt with $G_M = -2.496RT$ and -1.338RT, respectively, [20] nor as liquid amalgams such as Hg-K and Hg-Na with $G_M = -3.35RT$ and -3.23RT, respectively [21]. A close perusal of the figure also reveals that the energy parameters give a good representation of the experimental G_M as the computed values are in close agreement with experimental values for the alloys studied. In addition, the calculated activities using equation (9) are compared with the experimental activities in Table 2. The results presented in Table 2 show that there are good agreement between experimental and calculated activities. The close agreement obtained for G_M and activity gives us assurance to use the fitted interaction parameters (Table 1) to explain the nature of atomic interactions in the liquid alloys.

In principle, $S_{cc}(0)$ can be determined directly from small-angle diffraction experiments, but owning to experimental difficulty it has never been successfully accomplished. Hence, the need for theoretical determination of $S_{cc}(0)$. The experimental values of $S_{cc}(0)$ for the two systems were obtained by numerically differentiation of the measured free energy of mixing data through the middle term of Eqn. (9). This is usually referred to as experimental $S_{cc}(0)$ in literature [12]. The mixing behaviour of molten binary alloys can be deduced from the deviation of $S_{cc}(0)$ from the ideal $S_{cc}^{id}(0)$ value given by Eqn. (10). The presence of chemical order is indicated if $S_{cc}(0) < S_{cc}^{id}(0)$, while on the contrary, if $S_{cc}(0) > S_{cc}^{id}(0)$, the segregation and demixing take place in the liquid alloys. Fig. 2 shows the plot of concentration dependence of concentration-concentration fluctuations in the long wavelength limits for Cd-Ga and Cd-In liquid alloys, respectively. It is seen from the figures that computed $S_{cc}(0) > S_{cd}^{id}(0)$ throughout the entire concentration. This indicates homo-coordination, preference for

like atoms to pair as nearest neighbour in the alloys. It is also noticed that $S_{cc}(0)$ is symmetrical about equatomic composition $c_{Cd} = 0.5$ and there is a good agreement between the computed and the experimental data.

For the segregating systems, such as Cd-Ga and Cd-In, having size ratio values of 1.101 and 1.212, which are close to 1, the role of atomic size mismatch on their mixing properties can be neglected. On the other hand, examination of the ordered energy parameter, ω , revealed that $\omega = 0.115$ and 0.0418 for Cd-Ga and Cd-In alloys, respectively. This indicates that there is a higher tendency for like atoms to pair as nearest neighbour in the two molten alloys i.e. homo-pairs. As $\omega < 0$, indicates a tendency for unlike-atom to pairs, while $\omega > 0$ indicates tendency for like atoms to pair as perfectly disordered [7].

The variation of α_1 as a function of concentration is shown in Figure 3 for the two liquid alloys. Although, α_1 is positive across the whole concentration range as expected for segregated systems, as seen from the figure. A more careful study of this parameter signifies that the two alloys studied are weakly homocoordinated systems, as evident in the calculations of G_M /*RT* and $S_{cc}(0)$. However, the degree of segregation is more in Cd-Ga with ($\alpha_1^{max} = 0.0095$) at $c_{Cd} = 0.5$ than in Cd-In with ($\alpha_1^{max} = 0.0026$) at $c_{Cd} = 0.5$. One also notes that α_1 is symmetrical about equiatomic composition.

The diffusion coefficients (D_M/D_{id}) were computed via Eqn. (13). Evidently, it is seen that for ideal mixing, $S_{cc}(0) \rightarrow S_{cc}^{id}(0)$, i.e. $D_M D_s^{-1} \rightarrow 1$. The presence of chemical order is indicated by $D_M D_s^{-1} > 1$ as $S_{cc}(0) < S_{cc}^{id}(0)$. Likewise, $D_M D_s^{-1} < 1$ suggests the tendency for self-coordination, leading to phase segregation. From Fig. 4 which shows the plot of D_M / D_{id} versus concentration, it can be seen that the ratio D_M / D_{id} is less than 1 in the entire concentration range for the two alloys, which further corroborates earlier results that the degree of order in Cd-In is greater than in Cd-Ga alloy.

Using Eqns. (16) and (17), we have computed H_M and S_M , the results are shown in Figs. 5 and 6, respectively, as function of concentration. It is observed that the fit obtained for both enthalpy of mixing and entropy of mixing compared quite well with the experimental data, while the same could not be said for the enthalpy of mixing of Cd-Ga alloys. The values obtained (Table 1) show that the temperature dependence of the energy parameters are quite small and also that both the H_M and S_M for Cd-Ga and Cd-In alloys are symmetrical near the equiatomic composition and positive (typical of segregating systems) at all concentrations. Generally, one notes that both the experimental data and the theoretical values obtained using the interaction parameters and their temperature dependence is in close agreement.

Alloys	T(K)	Z	$\omega(eV)$	dω/dT	dβ/dT
Cd-Ga	700	10	0.1150	-	0
				0.00101	
Cd-In	800	10	0.0418	-	0
				0.00200	

Table 1: Values of Fitted Interaction Parameters for Molten Cd-Ga and Cd-In Alloys.

Table 2: Calculated and Experimental Activities Values for Cd-Ga and Cd-In Molten Alloys at 700 K and 800 K, respectively.

	Cd-Ga		Cd-In	
c _{Cd}	Theor y	Expt. ¹	Theor y	Expt. ¹
0.1	0.444	0.468	0.162	0.158
0.2	0.634	0.645	0.293	0.288
0.3	0.721	0.724	0.401	0.400
0.4	0.763	0.764	0.495	0.499
0.5	0.787	0.784	0.580	0.600
0.6	0.808	0.811	0.661	0.692
0.7	0.832	0.844	0.739	0.772
0.8	0.867	0.890	0.820	0.844
0.9	0.919	0.940	0.906	0.916



Fig. 1: Concentration dependence of free energy of mixing: G_M/RT for molten Cd-Ga and Cd-In alloys at 700 K and 800 K, respectively. The solid line denotes theoretical values while the times and stars denote experimental data for Cd-Ga and Cd-In alloys at respective temperatures. c_{Cd} is the concentration of Cd in the alloy. The experimental data were taken from [15].



Fig. 2 : Concentration-concentration fluctuations in the long-wavelength limits, S_{cc} (0), for molten Cd-Ga and Cd-In alloys at 700 K and 800 K, respectively. The solid line denotes theoretical values while the times and stars denote experimental data for Cd-Ga and Cd-In alloys at respective temperatures and the dots denote ideal S_{cc}^{id} (0). c_{Cd} is the concentration of Cd in the alloy.



Fig. 3 : Calculated Warren-Cowley short range order parameter, $\alpha 1$, via Eqn. (12) for molten Cd-Ga and Cd-In alloys at 700 K and 800 K, respectively.



Fig. 4 : Calculated chemical diffusion via Eqn. (13) for molten Cd-Ga and Cd-In alloys at 700 K and 800 K, respectively.



Fig. 5 : Concentration dependence of enthalpy of mixing: H_{M}/RT for molten Cd-Ga and Cd-In alloys at 700 K and 800 K, respectively. The solid line denotes theoretical values while the times and stars denote experimental data for Cd-Ga and Cd-In alloys at respective temperatures. c_{Cd} is the concentration of Cd in the alloy. The experimental data were taken from [15].



Fig. 6 : Concentration dependence of entropy of mixing: S_M / RT for molten Cd-Ga and Cd-In alloys at 700 K and 800 K, respetively. The solid line denotes theoretical values while the times and stars denote experimental data for Cd-Ga and Cd-In alloys at respective temperatures. c_{Cd} is the concentration of Cd in the alloy. The experimental data were taken from [15].

4.0 Concluding Remarks

The alloying behaviour of Cd-Ga and Cd-In molten alloys have been analyzed by the QCAM, taken into account the effects of atomic size mismatch ratio on the various thermodynamic properties investigated. Our theoretical analysis reveals that there is a higher tendency for like atoms to pair as nearest neighbour in the two molten alloys investigated (i.e. homo-coordination) as the concentration of Cd increases across the concentration range. However, thermodynamic properties of both systems indicate that the degree of atomic order is more in Cd-In than in Cd-Ga alloy.

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