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Original Research Article

Effects of surface coordination of atoms on the surface properties of Cd-X (X= Ga, Zn) liquid alloys

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Abstract:

We have investigated the effect of surface coordination of atoms on the surface properties of Cd-Ga and Cd-Zn liquid alloys by varying their surface coordination fractions using statistical mechanics model. Surface tension and surface concentration did not have significant effect on the calculation of both surface tension and surface concentration of two alloys. The computation of the concentration fluctuations at the surface revealed that it was sensitive to the surface coordination fractions of both segregating systems. In those alloys we found that the computation of the Warren-Cowley short rang order parameter was influenced by the surface coordination fractions.

Keywords: surface segregation, surface coordination fraction, surface tension, surface concentration-concentration fluctuation

Introduction

In addition to the interest in investigating the bulk properties of liquid binary alloys, much effort have been made towards understanding the surface phenomenon, which is of remarkable relevance not only academic interest but more importantly because of its many technological applications such as catalysis, corrosion, thin properties etc. (Prasad et al, 1998; Cheng,1983). Surface segregation is usually indicated by the preferential enrichment of the surface atoms of one of the two component elements in binary alloys. It has also been regarded as a phenomenon which manifests itself as a difference in composition between the surface and bulk or between an interface and the adjoining phases (Patrick et al, 1989; Prasad and Singh, 1991; Wynblatt and Ku, 1977). On the basis of quasi-chemical theory, the constituents in the alloys with lower vaporization segregates at the surface; another theory holds that elements with lower surface energy will be enriched on the surface; according to strain theory, the constituent with larger atomic size segregates at the surface in order to minimize the strain energy (Cheng,1983; Kumar et al, 1979; Wynblatt and Ku, 1977). Surface segregation has been explained in terms of heat of solution and bond breaking theory (Hamilton 1979; Moran-Lopez and Falicov, 1978).It has been established that segregation may occur not merely for topmost layer of a surface, but for many atomic layers from the surface(Vahalia,1986). Also surface relaxation has been reported to play a dominant role in determining the surface composition (Vahalia, 1986; Williams and Nason, 1974). In fact, it has been assumed that the bond strengths are related to the number of nearest neighbors of an atom, and hence, the strengths differ at a surface from that in the bulk (Donnely and King, 1978).These assumed connection between the surface relaxation and the number of nearest neighbors of atom possibly informed the reason why Prasad and Singh (Prasad and Singh, 1991) and Novakovic et al (Novakovic et al, 2002) independently suggested that the p and q, which are the fraction of the total next neighbor contact made by a molecule within its own layer and that in either adjoining layer usually taken as p =0 .5 and q = 0.25 be treated as parameters in viewed of the disordered structure and relaxation effects. That p and q should not be restricted to values 0.5 and 0.25 respectively, which was supported by Oguchi et al (1981), where they reported that in the treatment of Hoar and Melford the values of p and q can be slightly varied by some relaxation effect of the surface layer and thus they employed $p = 0.75$ instead of $p = .05$ as Hoar and Melford did on 1957. Consequently, the choice of $p = 0.5$ and $q = 0.25$ is usually based on the assumption of closed-packed structures at the liquid surface. Because of the relaxation effect and lack of complete information on the structures of binary liquid surfaces, *p* and *q* may still take values different from 0.5 and 0.25 respectively. In addition, it is noted that the kind of surface assumed or chosen may determine how the atoms are arranged at the surface of the liquid. Arising from the aforementioned, the focus of this article is to vary *p* and *q* and attempt quantifying the effects by way of comparing the results with that of their usual values when close-packed structure is assumed.

Theoretical formalism

Surface tension and surface concentration

On the basis of the concept of the layered structure near the interface, the relationship between bulk and surface properties using a statistical mechanics approach has been established (Prasad and Singh,1991).The pair of equation relating the surface tension and surface concentration for binary liquid alloys is expressed as:

$$\tau = \tau_A + \frac{k_B T}{\xi}\ln\frac{C_A^s}{C_A^b} - \frac{k_B T}{\xi}\ln\gamma_A + \frac{\omega}{\xi}\left[p\left(C_B^s\right)^2 + q\left(C_B^b\right)^2\right] \quad \text{---------- 1 (a)}$$

$$\tau = \tau_B + \frac{k_B T}{\xi}\ln\frac{C_B^s}{C_B^b} - \frac{k_B T}{\xi}\ln\gamma_B + \frac{\omega}{\xi}\left[p\left(C_A^s\right)^2 + q\left(C_A^b\right)^2\right] \quad \text{---------- 1 (b)}$$

Where τ_A and τ_B are the surface tension values for the pure components A and B respectively; T is the temperature of interest in Kelvin; C_i^b and C_i^s are the bulk and surface concentrations of the alloy components (i = A, B); *p* and *q* are the surface coordination fractions, which are defined as the fraction of the total number of nearest neighbors made by atom within its own layer and that in the adjoining layer. For *p* and *q*, the following relation is available, $p + 2q = 1$ and for usually assumed close-packed structure, $p = 0.5$ while $q = 0.25$; ξ is the mean atomic surface area whose value is usually obtained from the relation:

$$\xi = \sum C_i \xi_i \qquad (i = A, B) \qquad \text{---------- 2}$$

Where the atomic area of hypothetical surface for each component ξ_i is given as (Prasad and Singh,1991).

$$\xi_i = 1.102\left(\Omega_i / N_0\right)^{2/3} \qquad \text{---------- 3}$$

Ω_i is the molar volume of the species i and N_0 stands for Avogadro number; and γ_B are the bulk activity coefficients of the alloy components.

$$\gamma_A = \left[\frac{\beta^b + C_A^b - C_B^b}{C_A^b(1+\beta^b)}\right]^{\frac{Z^b}{2}} ; \ \gamma_B = \left[\frac{\beta^b - C_A^b + C_B^b}{C_B^b(1+\beta^b)}\right]^{\frac{Z^b}{2}} \quad \text{---------- 4}$$

with

$$\beta^b = \left[1 + 4C_A^b C_B^b\{\exp(2\omega / Z^b k_B T) - 1\}\right]^{\frac{Z^b}{2}} \quad \text{---------- 5}$$

Where ω is the order energy and Z^b, the coordination number in bulk.

Surface concentration fluctuations and Warren-Cowley short range order parameter

A microscopic function, very useful for describing the nature of mixing of binary liquid alloys like chemical order and segregation, is the concentration fluctuation while the degree of chemical order and segregation are usually quantified by another microscopic function, called Warren-Cowley short range order parameter (Warren, 1996; Cowley, 1950). An expression for the concentration fluctuation at the surface, obtained by solving the surface grand partition function based on the earlier works of Prasad and Singh, (1991) and Prasad et al, (1998) for the bulk phase in the framework of quasi-chemical approximation for the regular solution is:

$$S_{cc}^s(0) = C_A^s C_B^s [1 + Z^s(1-\beta^s)/2\beta^s]^{-1} \quad \text{---------- 6}$$

Here β^s is the function obtained from β^b by substituting C^s and Z^s in place of C^b and Z^b; surface coordination number, Z^s, is given by the relation: $Z^s = Z^b(p+q)$.
If the constituent atoms are mixed ideally (i.e. ω = 0), the equation becomes:

$$S_{cc}^s(0, \text{ideal}) = C_A^s C_B^s \quad \text{---------- 7}$$

The bulk expressions equivalent of the above surface expressions for concentration fluctuations are given by:

$$S_{cc}^b(0) = C_A^b C_B^b [1 + Z^b(1-\beta^b)/2\beta^b]^{-1} \quad \text{---------- 8}$$

and

$$S_{cc}^b(0, \text{ideal}) = C_A^b C_B^b \quad \text{---------- 9}$$

The surface Warren-Cowley short range order parameter, $\boldsymbol{\alpha_1^s}$, is related to the surface concentration fluctuations, $\boldsymbol{S_{cc}^s(0)}$, as given by the expression:

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$$\frac{S_{cc}^{s}(0)}{C_A C_B} = \frac{1+\alpha_1^s}{1-(Z^s-1)\alpha_1^s} \quad \text{---------- 10}$$

This is deduced from the expression for the bulk Warren-Cowely short range order parameter, $\boldsymbol{\alpha}_1^b$, given by:

$$\frac{S_{cc}^{b}(0)}{C_A C_B} = \frac{1+\alpha_1^b}{1-(Z^b-1)\alpha_1^b} \quad \text{---------- 11}$$

Results and Discussion

The ordering energy, ω, the temperature dependent quantity has been used as input energy parameter for the calculation of various bulk as well as surface properties for liquid alloys Cd-Ga and Cd-Zn at temperatures 750 K and 800 K respectively. It can be estimated from experimental value of excess free energy of mixing, G_M^{XS}, (Hulgren et al, 1973) through standard thermodynamic expression for equiatomic composition (Singh et al, 1990; Koirala et al, 2014).

For this, we have:

$$\frac{G_M^{XS}}{Nk_BT} = \ln 2^{Z/2}[1+\exp(-\omega/Zk_BT)]^{-z/2} \quad \text{---------- 12}$$

Here Z is the coordination number, Neutron and X-ray diffraction experiment confirm a random distribution of atoms in a closed-packed structure and suggest that for molten binary alloys, Z could be taken as equal to 10. The best fit values of ω for the liquid alloys are given in Table (1):

Table 1. Basic parameters obtained from bulk properties calculation for Cd-Ga and Cd-Zn at temperatures 700 K and 800 K respectively.

Alloys	Temperature	ω
Cd-Ga	700 K	1.85 k_BT
Cd-Zn	800 K	1.24 k_BT

Surface tension and surface concentration

For the computation of surface properties of alloys, under the assumption of closed-packed structure, the surface coordination number *p* and *q* are taken as 0.5 and 0.25 respectively. However, in view of the disordered structure and relaxation effect of the surface layer we have attempted treating *p* and *q* as parameters by varying their values. Thus we have chosen to vary the values of *p* in the range 0.25-1.0 and the corresponding values of *q* obtained from the relation $p+2q=1$. The various value of *p* and the corresponding values of q as used in this work are shown in Table 2.

Table 2. Various values of surface coordination fractions used in our calculation of surface properties for Cd-Ga and Cd-Zn at temperatures 700 K and 800 K respectively.

p	q
0.250	0.375
0.500	0.250
0.667	0.167
0.750	0.125
1.000	0.000

Table 3. Essential parameters for the surface properties calculations*

Atoms	M.P.(K)	τ(N/m)	dτ/dT(mN/mK)
Cd	594.0	570	-0.026
Ga	302.8	718	-0.100
Zn	692.0	782	-0.170

*Brandes & Smithells, 1983

Subtracting Eq.1 (b) from 1(a), the obtained equation has been solved numerically, yielding the values of surface concentration, C_i^s. The surface tension of liquid alloys can be computed by substituting these values into either Eq.1 (a) or 1(b). For this, we need experimental data of density and surface tension of the components at the working temperature. We calculated the density and surface tension for the components of that alloys at their working temperatures by using the equations as:

$$\rho(T) = \rho_0 + (T - T_0)\frac{d\rho}{dT} \quad \text{---------- 13}$$

$$\tau(T) = \tau_0 + (T - T_0)\frac{d\tau}{dT} \quad \text{---------- 14}$$

Where T and T_0 are respectively the temperature of investigation and melting temperature; $\frac{d\rho}{dT}$ and $\frac{d\tau}{dT}$ represent the temperature coefficient of density and surface tension respectively for component metal of the alloys. The required input parameters for the calculation are given in Tables 1-3.

In Figures 1(a,b) and 2(a,b),we observed that plots of τ and C^S for Cd-Ga and Cd-Zn liquid alloys follow the usual pattern of negative deviation of τ from the

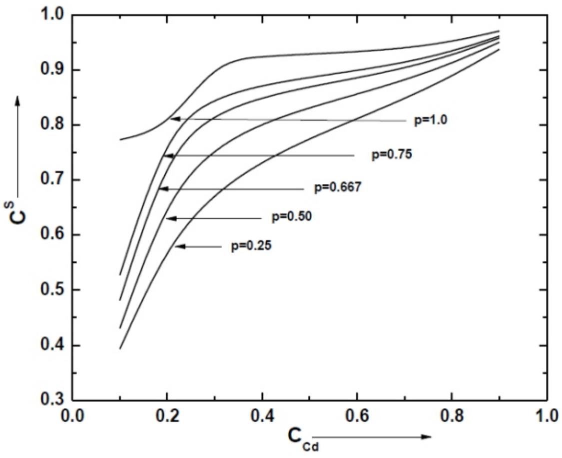

Figure 1. (a) The computed value of surface concentration (C^S) verses bulk concentration of Cd (C_{Cd}) for Cd-Ga at 700 K and at different values of surface coordination fractions

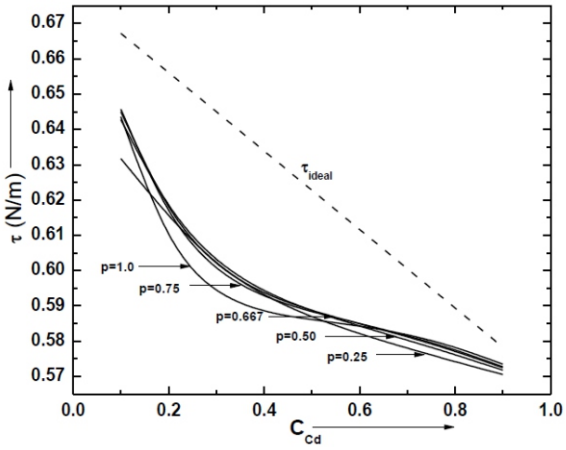

Figure 1. (b) The computed value of surface tension (τ) verses bulk concentration of Cd (C_{Cd}) for Cd-Ga at 700 K and at different values of surface coordination fractions.

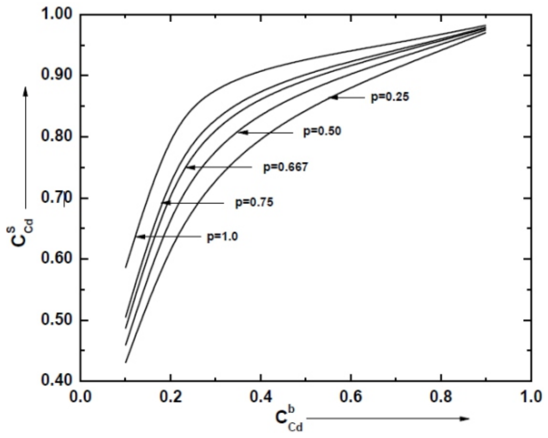

Figure 2. (a) The computed value of surface concentration (C^S) verses bulk concentration of Cd (C_{Cd}) for Cd-Zn at 800K and at different values of surface coordination fractions.

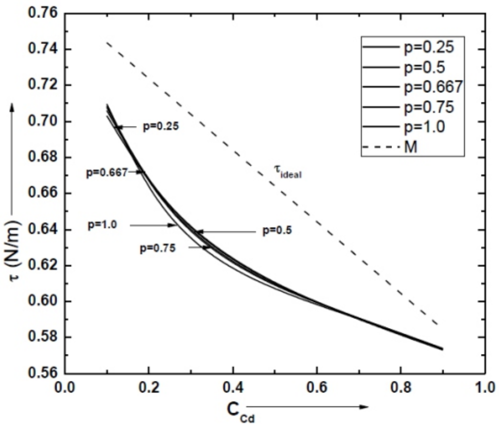

Figure 2. (b) The computed value of surface tension (τ) verses bulk concentration of Cd (C_{Cd}) for Cd-Zn at 800K and at different values of surface coordination fractions.

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Proportional mathematical addition of the pure components surface tension and increasing C^S as a bulk concentration increases immaterial of the value of *p*. These show that the liquid surface of each of the systems is enriched with the component of lower surface tension, immaterial of the assumed structure of the liquid surface.

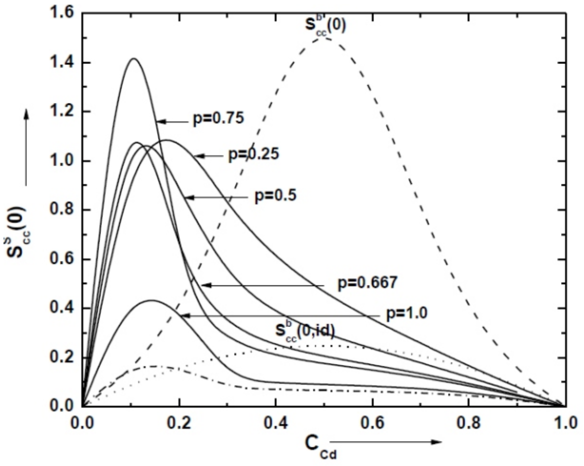

Figure 3.(a) The computed value of surface concentration fluctuation ($S_{cc}^S(0)$) verses bulk concentration of Cd (C_{Cd}) for Cd-Ga at 700 K and at different values of surface coordination fractions.

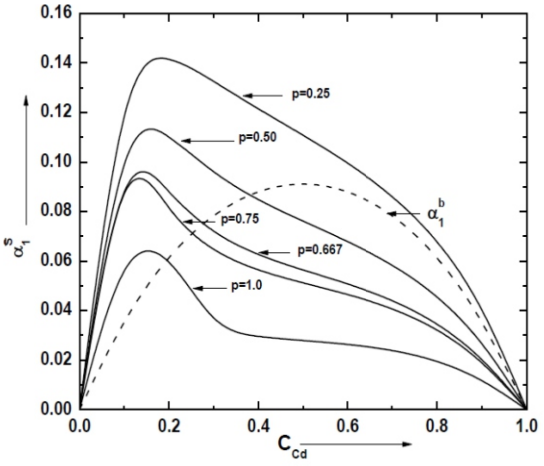

Figure 3. (b) The computed value of surface short range order parameter (α_1^S) verses bulk concentration of Cd (C_{Cd}) for Cd-Ga at 700 K and at different values of surface coordination fractions.

Surface concentration fluctuations and Warren-Cowley short range order parameter

Equations (4) and (8) have been employed to calculate the concentration fluctuations at the surface and Warren-Cowley short range parameter at the surface, respectively, for the liquid alloys Cd-Ga and Cd-Zn. Figures 1(c,d) and 2(c,d) show the plot of S^S_{CC} (0)and α_1^s for the two alloys.

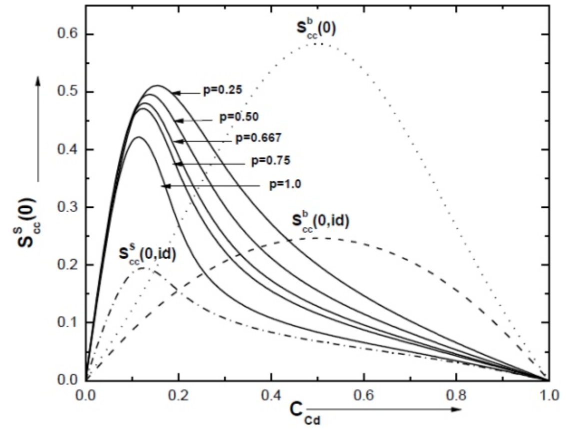

Figure 4. (a) The computed value of surface concentration fluctuation ($S_{cc}^S(0)$) verses bulk concentration of Cd (C_{Cd}) for Cd-Zn at 800 K and at different values of surface coordination fractions.

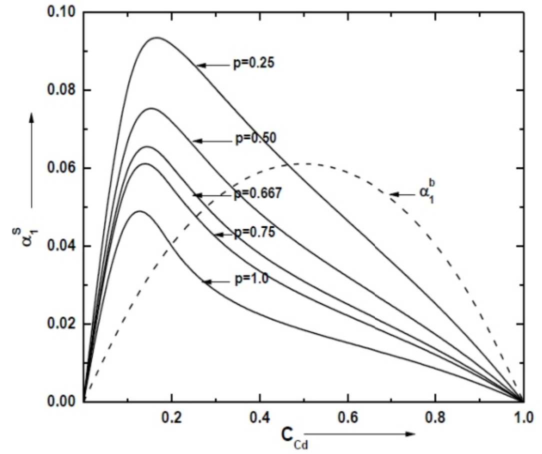

Figure 4. (b) The computed value of surface short range order parameter (α_1^S) verses bulk concentration of Cd (C_{Cd}) for Cd-Zn at 800 K and at different values of surface coordination fractions.

Although, the profile reveal that each of the two systems has the homo-coordination tendency since they have their ${}_{scc}S(0)$ greater than ${}_{scc}S(0,id)$ and α_1^s being positive throughout the bulk concentration immaterial of the values of *p*, yet we observed significant deviations in the profiles for each of the two alloys at various values of *p*. This indicate that the choice of p has significant effect on the ${}_{scc}S(0)$ and α_1^s of the two alloys. Also, we observed that in both alloys the profiles of at various *p* shows that the degree of segregation increases with decreasing p values.

Conclusions

We have used a statistical approach to investigate the effects of surface coordination of atoms on the surface properties of Cd-Ga and Cd-Zn liquid alloys respectively at temperatures 700 K and 800 K by varying the values of surface coordination fractions p and q. Our study reveals, atom with smaller value of surface tension segregates at the surface in the preference to the other component with larger value of surface tension, with a view to minimize the total energy. The noticable remarks are found as :

(a) The choice of p and invariably q has a significant effect on surface concentration but not significant effect on the surface tension of Cd-Ga and Cd-Zn alloys, which are both segregating systems.

(b) The choice of p and invariably q has a significant effect on the surface concentration fluctuations and surface short range order parameters of Cd-Ga and Cd-Zn alloys, which are both homo-coordination systems.

Consequently, although we do not have access to the surface experimental data for most of the systems we studied to compare our results; we are of the opinion that our computed results are reliable. This is on premise that in our calculations we employed the experimentally fitted value of ordering energy parameter obtained from bulk properties calculations for the respective alloys.

References

Brandes EA and Smithells CJ. Metals Reference Book. Sixth Edition, 1983, 14-6.

Cheng Y. Physical origin of surface segregation in binary liquid alloys. Phys Rev B, 1983, 28 29-37.

Cowley JM. An approximate theory of order in alloys. Phys Rev, 1950, 77, 669.

Donnelly RG and King TS. Surf Sci,1978, 74, 89.

Hamilton JC. Prediction of surface segregation in binary alloys using bulk alloy variables. Phys Rev Lett 1979, 42(15), 989.

Hoar TP and Melford DA.Trans Faraday Soc., 1957, 315.

Hultgren R, Desai PD, Hawkins DT, Gleiser M, Kelley KK. Selected Values of the Thermodynamic Properties of Binary Alloys. ASM Metals Park, Ohio, 1973, 10-13.

Koirala I, Singh BP and Jha IS. Transport and surface properties of molten Cd-Zn alloys. JIST, 2014, 19(1) 14.

Kumar V, Kumar D and Joshi SK. Surface Segregation in alloys. Phys Rev B,1979, 19(4),1954.

Moran-Lopez JL and Falicov LM. Theory of surface effect in binary alloys -ordering alloys. Phys Rev B, 1978, 18(6), 25-42.

Novakovic R, Ricci E, Giuranno D and Gnecco F. Surface properties of Bi-Pb liquid alloys. Surf Sci, 2002, 515, 377.

Oguchi Y, Itami T and Simoji M. Surface tension of liquid Hg-In liquid alloys. Phys Chem Liqd, 1981, 10, 315. .

Patrick RS, Chen AB, Sher A and Berding MA. Surface segregation in psedobinary alloys. Phys Rev B, 1989, 39(9), 59-80.

Prasad LC and Singh RN. Surface segregation and concentration fluctuation at the liquid-vapour interface of molten Cu-Ni liquid alloys. Phys Rev B,1991, 44,137-68.

Prasad LC, Singh RN, Singh VN and Singh GP. Correllation between bulk and surface properties of Ag-Sn liquid alloys. J.Phys.Chem.B,1998,102,921.

Singh RN, Mishra IK, Singh VN. Local order in Cd-based liquid alloys. Phys Condens, Matter, 1990 2: 8457.

Vahalia U, Dowben P and Miller A. J Vac Sci Technol A, 1986, 4(3), 1675.

Warren BE. X-ray Diffraction. Addison-Wesle, Reading MA. 1996, 227.

Williams FL and Nason D. Surf Sci, 1974, 45, 377.

Wynblatt P and Ku RC. Surface energy and solute strain energy effect in surface segregation. Surf Sci, 1977, 65, 511.