

Transport and Surface Properties of Molten Cd-Zn Alloys

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ABSTRACT

Simple statistical theory has been used to report the thermo-physical properties of mixing in liquid Cd-Zn alloys. The energetic of mixing in liquid alloys has been analyzed through the study of surface properties (surface tension, surface concentration) and transport properties (diffusivity, viscosity). Negative deviation from Raoultian behaviour has been observed in the computed mixing parameters (viscosity, surface tension) of the alloys. The computed results support a weak phase-separation tendency in molten Cd-Zn system.

Key words: Thermo-physical properties, Raoultian behavior, diffusivity, surface segregation

INTRODUCTION

Alloys are industrial or commercial materials, which are grown from molten state. Liquid alloys are disordered materials which have short range order. Properties of disordered materials are much more difficult to understand than those of crystals and the complexity in the properties of mixing of binary liquid alloys is less understood. Therefore, the study of the properties of binary liquid alloys demands extensive theoretical investigations. Theoreticians have long been attempting to understand the properties of liquid alloys on the basis of the interactions between atoms or molecules (Flory, 1942; Gugenheim, 1952; Harrison, 1966; Lebowitz, 1964; Faber, 1972; Shimoji, 1977; Bhatia *et al.* 1973; Alonso & March, 1982; Bernu *et al.* 1987; Li & Tosi, 1989; Singh *et al.* 1990 & 1993; Singh & Sommer, 1992; Novakovic, 2010).

Metal alloys are generally more beneficial over metals in various fields of technology such as engineering and metallurgical science for their increased mechanical strength, heat resistance, chemical resistance, decreased production costs, and wide range of colours. Cadmium is highly reactive metal in group IIB of periodic table. Compounds and alloys of this group have been widely used in fabricating solid state electronic components. Cadmium is used in many types of solder for standard electromotive force cells, Ni-Cd batteries, pigments, coatings, stabilizers and as barrier to control atomic fission. It is also used in electroplating of automotive, aircraft and in photoelectric cell in fire protection systems (Koirala *et al.* 2013). Cadmium-zinc is one of the numerous metal alloys, which has potential applications in bearing assemblies, ballasts, casting, step soldering, radiation soldering etc. Small content of cadmium lowers the melting point of cadmium-zinc alloys, improves thermal and electrical conductivities

and increases mechanical properties such as hardness, wear resistance, tensile and fatigue strength (Adhikari *et al.* 2013).

The knowledge of transport properties such as diffusivities and viscosities of the metals in the liquid phase are required for many metallurgical processes and heterogeneous chemical reactions. On the other hand, knowledge of surface properties is essential for understanding of the surface related phenomenon such as corrosion, welding, casting, gas absorption, wetting characteristics of solders and kinetics of phase transformation (Prasad *et al.* 1991).

In the present work, we intend to explain the alloying behavior of Cadmium-Zinc liquid alloy on the basis of simple statistical model (Singh *et al.* 1990). It is a statistical mechanical model in which the grand partition function is used to obtain analytic expressions for the conditional probabilities enumerating the occupation of two neighbouring sites by the atoms of the constituent elements in terms of the ordering energy. The ordering energy, an important input parameter, is used for all calculation which is temperature dependent. We study the concentration dependent thermo-physical properties of mixing of liquid Cd-Zn alloys at 800K. The energetic of mixing as well as the negative deviation from Raoultian behavior for transport and surface properties has been discussed. It is known that for segregating alloys the size effects have an appreciable influence on their surface properties (Singh & Sommer, 1992). The degree of effects increases together with a preference of a system toward phase separation.

MATERIALS AND METHODS

Transport properties

The transport properties such as viscosity, chemical diffusion coefficients etc may help to gain knowledge

about the mixing behaviour of binary liquid alloys at the microscopic level. Viscosity (η) of liquid alloys is equally important in the understanding of the atomic level structure and interactions. As in the case of thermodynamic functions, the composition dependence of η of liquid alloys is also found to exhibit either a linear variation, or positive or negative deviations from the linear law. A simple formula for the investigation of viscosity of a binary solution is

$$\eta = \eta_{id} \left[1 - x(1-x) \left(\frac{2\omega}{k_B T} \right) \right] \dots\dots\dots (1)$$

But, $\eta_{id} = x\eta_A^0 + (1-x)\eta_B^0 \dots\dots\dots (2)$

where η_i^0 is the viscosity of pure component i , ω is the interchange energy or order energy and x , the concentration of the components (Moelevyn-Hughes, 1964).

The mixing behaviour of the alloy forming molten metals can also be studied at the microscopic level in terms of coefficient of diffusion. The mutual diffusion coefficient (D_M) of binary liquid alloys can be expressed in terms of activity (f_i) and self- diffusion coefficient (D_{id}) of pure component with the help of Darken’s equation (Darken & Gurry, 1953).

$$\frac{D_M}{D_{id}} = \frac{d \ln f_i}{dx_i} \dots\dots\dots (3)$$

Considering only the energetics of the nearest-neighbour bond, we obtain an expression for D_M

$$\frac{D_M}{D_{id}} = \left[1 - x(1-x) \left(\frac{2\omega}{k_B T} \right) \right] \dots\dots\dots (4)$$

with $D_M = xD_B + (1-x)D_A \dots\dots\dots (5)$

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

The ratio D_M/D_{id} indicates the mixing nature of molten alloys; $D_M /D_{id} < 1$ indicates the tendency of homo-coordination while $D_M /D_{id} > 1$ indicates the tendency of hetero-coordination and D_M/D_{id} approaches 1 for ideal mixing (Guggenheim, 1952; Darken & Gurry, 1953; Singh & Sommer, 1992).

Surface properties

For the processing of materials and productions in the metallurgical industry, knowledge of surface phenomena like surface segregation and surface tension is essential. It has been noted that many properties of physical relevant such as mechanical behaviour, kinetics of phase transformation, catalytic activity of alloy catalyst and thin film can not be explained without understanding

surface phenomena. Surface segregation results from the interaction among the atoms and surface tension, is the enrichment of the surface by the atoms of the particular component element in a binary alloy (Prasad *et al.* 1991 & 1998). In the statistical formulation of Prasad *et al.* (1991 & 1998) binary liquid alloy is considered to have a layered structure near the surface with thermodynamic equilibrium existing between the species at the surface and in the bulk. The surface properties of liquid alloys are influenced by their bulk thermodynamic properties. The surface grand partition function is related to the surface tension τ by the expression (Prasad *et al.* 1991 & 1998).

$$\Xi^s = \exp \left(\frac{-S\tau}{k_B T} \right) = \exp \left(\frac{-N^s \tau \xi}{k_B T} \right) \dots\dots\dots (6)$$

where S is the surface area and ξ is the mean area of the surface per atom and is defined as $\xi = S/N^s$, and N^s is the total number of atoms at the surface. k_B is the Boltzmann constant.

A pair of equation for surface tension of the binary liquid alloys in terms of activity coefficient (γ_i) of the alloy components and interchange energy parameter (ω), at the given temperature T , proposed by Prasad *et al.*, have been reduced in the simple form, using zeroth approximation as

$$\tau = \tau_A + \frac{k_B T}{\xi} \ln \frac{x^s}{x} + \frac{\omega}{\xi} \left[p(1-x^s)^2 + (q-1)(1-x)^2 \right] \dots\dots 7(a)$$

$$\tau = \tau_B + \frac{k_B T}{\xi} \ln \frac{(1-x^s)}{(1-x)} + \frac{\omega}{\xi} \left[p(x^s)^2 + (q-1)(x)^2 \right] \dots\dots 7(b)$$

where τ_A and τ_B are the surface tension values for the pure components A and B respectively; x and x^s are the bulk and surface concentrations of the alloy component; 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 (Prasad *et al.* 1991 & 1998; Novakovic *et al.* 2005; Novakovic, 2010).

$$P + 2q = 1$$

For closed packed structure, $p = 0.5$ while $q = 0.25$ (in view of the disordered structure and relaxation effect of the surface layer p and q should be treated as parameters (Prasad *et al.* 1991)).

The pair of equations 20(a) and 20(b) can be solved numerically to obtain x^s as a function of x . Obviously the surface concentration depends upon the surface tension of the i^{th} component in the pure state (τ_i), surface area per atom(ξ), order energy(ω) and the coordination

fractions (p and q). This approach is useful because it can be used to investigate the dependence of surface composition on order energy and surface coordination.

The mean atomic surface area ξ ($=A/N^s$) is given as

$$\xi = \sum c_i \xi_i \quad (i = A, B) \dots\dots\dots(8)$$

Where the atomic area of hypothetical surface for each component is given as (Prasad *et al.* 1988) :

$$\xi_i = 1.102 \left(\frac{\Omega_i}{N_0} \right)^{2/3} \dots\dots\dots(9)$$

where Ω_i is the molar volume of the species i and N_0 stands for Avogadro number.

On the basis of assumption of monatomic surface layer, Butler's approach (Butler, 1932) of surface tension τ of liquid solution can be expressed as

$$\tau = \frac{\mu_A^s - \mu_A^b}{\alpha_A} = \frac{\mu_B^s - \mu_B^b}{\alpha_B} = \dots\dots = \frac{\mu_i^s - \mu_i^b}{\alpha_i} \dots\dots\dots(10)$$

Where μ_i^s, μ_i^b and α_i represent respectively the chemical potential in the hypothetical surface and that in the bulk and molar surface area of pure component i (A or B).

Equation (10) yields the expressions for surface tension in terms of partial excess free energy of mixing in bulk ($G_i^{E,b}$) and at the surface ($G_i^{E,s}$) and concentration in the bulk (x) and at the surface (x^s) as

$$\tau = \tau_A + \frac{1}{\alpha_A} (G_A^{E,s} - G_A^{E,b}) + \frac{RT}{\alpha_A} \ln x^s - \frac{RT}{\alpha_A} \ln x \dots\dots 11(a)$$

$$\tau = \tau_B + \frac{1}{\alpha_B} (G_B^{E,s} - G_B^{E,b}) + \frac{RT}{\alpha_B} \ln(1-x^s) - \frac{RT}{\alpha_B} \ln(1-x) \dots\dots 11(b)$$

where τ_A and τ_B are surface tension of pure component A and B respectively.

The area of monatomic surface layer for the component i can be calculated by the relation (Butler, 1932).

$$\alpha_i = 1.091 N_0^{1/3} \Omega_i^{2/3} \dots\dots\dots(12)$$

Where N_0 is Avogadro's number and Ω_i stands for molar volume of the component i , can be calculated from its molar mass and density.

RESULTS AND DISCUSSION

The ordering energy, ω , the temperature dependent quantity has been used as input energy parameter for the calculation of diffusivity, viscosity and surface tension for Cd-Zn liquid alloys at 800K. It can be estimated from experimental value of excess free energy of mixing (G_M^{XS}) through standard thermodynamic expression for

equiatomic composition (Singh *et al.* 1990; Koirala *et al.* 2013). For this, we have

$$\frac{G_M^{XS}}{Nk_B T} = \ln 2^{z/2} [1 + \exp(-\omega/zk_B T)]^{-z/2} \dots\dots\dots(13)$$

From equation (13), the best fit value for ω is found to be

$$\frac{\omega}{k_B T} = +1.24 \dots\dots\dots(14)$$

The positive value of energy parameter ($\frac{\omega}{k_B T}$) suggests

that there is higher tendency for like atoms to pair in the alloy which implies a homo-coordination system. However, the tendency of pairing is weak since energy parameter is small.

The ratio of the mutual and intrinsic-diffusion coefficients ($\frac{D_M}{D_{id}}$) as a function of concentrations, has

been calculated using the equation (4). The plot of $\frac{D_M}{D_{id}}$

verses concentration of cadmium in Cd-Zn system is shown in Fig.1. The obtained diffusivity for the alloys system shows the values of $\frac{D_M}{D_{id}} < 1$ over the entire range

of concentration which is indicative for the phase separation in the mixture. A minimum value of $\frac{D_M}{D_{id}} =$

0.38 for $x_{Cd} = 0.5$, confirms a weak tendency for segregation.

The viscosity of the Cd-Zn liquid alloy has been computed numerically from equation (1). The plot of η verses bulk concentration of x_{Cd} in Cd-Zn liquid alloy is shown in Fig.2. In Fig. 2 small negative deviations from the linear law (Raoult's law) in viscosity isotherms $\eta(c)$ have been observed for the regular alloy which is the indicative of segregating system.

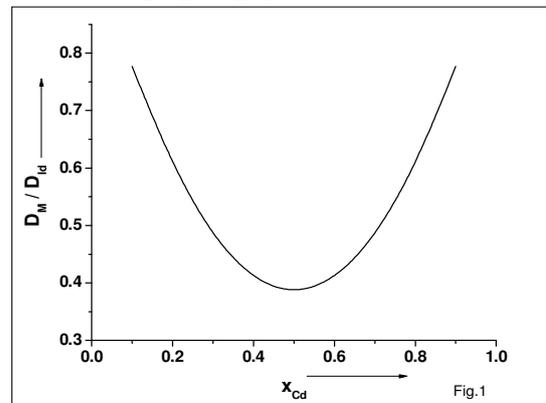


Fig. 1. Ratio of mutual and intrinsic diffusion coefficients (D_M/D_{id}) Vs concentration of cadmium (x_{Cd}) in liquid Cd-Zn alloy at 800K.

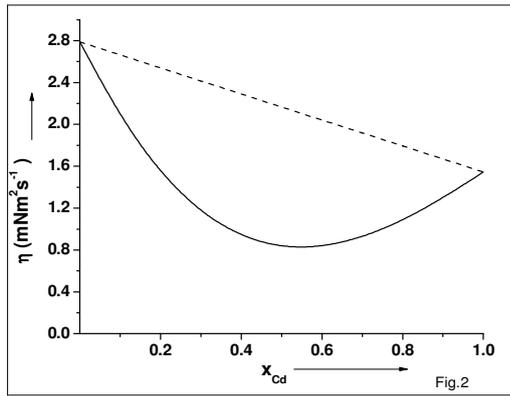


Fig. 2. Viscosity (η) Vs concentration of cadmium (x_{Cd}) in liquid Cd-Zn alloy at 800K .

The surface concentrations and surface tension of Cd-Zn have been computed numerically from the equations 7(a) and 7(b), where interchange energy, ω is used instead of γ_A and γ_B as used in Prasad’s model. For this, we need experimental data of density and surface tension of the components at the working temperature. We have calculated the density and surface tension for the components Cd and Zn (Iida & Guthrie, 1988; Brandes & Smithells, 1983) at the working temperature $T=800K$ by using the following equations

$$\rho_{Cd}(T) = 8.709 - 1.16 \times 10^{-3}T \dots\dots\dots 15(a)$$

$$\rho_{Zn}(T) = 7.336 - 1.1 \times 10^{-3}T \dots\dots\dots 15(b)$$

$$\tau_{Cd}(T) = 0.5854 - 0.26 \times 10^{-4}T \dots\dots\dots 16(a)$$

$$\tau_{Zn}(T) = 0.8996 - 1.7 \times 10^{-4}T \dots\dots\dots 16(b)$$

The mean atomic surface area ξ has been calculated by using equations (8) and (9). For calculating surface tension we used same estimated energy parameter, ω . At first, surface concentrations of cadmium in alloy Cd-Zn have been obtained as a function of bulk concentration by concurrently solving the equations 7(a) and 7(b). Using the obtained values of surface concentrations we computed the surface tension of Cd-Zn liquid alloys at temperature 800K for whole concentration range.

For the computation of surface concentration and surface tension of the Cd-Zn alloy on using Butler’s approach, the partial excess free energies of mixing of pure components of the alloys have been taken from the ref.(Hultgren *et al.* 1973). By concurrently solving the equations 11(a) and 11(b), surface concentrations of Cd in alloy Cd-Zn have been obtained as a function of bulk concentration and then using the obtained values of surface concentrations we computed the surface tension of Cd-Zn liquid alloys at temperature 800K for whole concentration range.

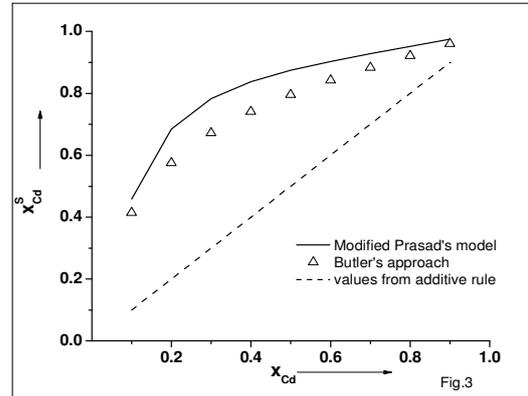


Fig. 3. Surface concentration of cadmium (x_{Cd}^S) Vs bulk concentration of cadmium (x_{Cd}) in liquid Cd-Zn alloy at 800K .

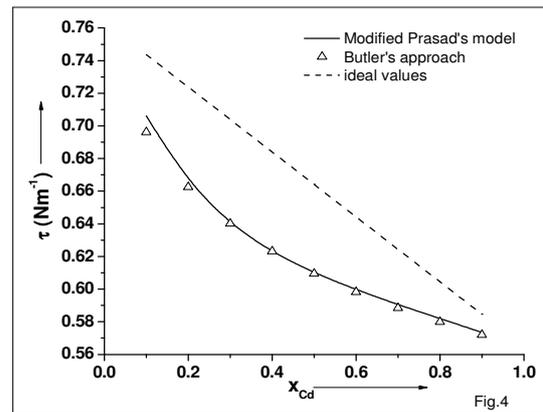


Fig. 4. Surface tension (τ) Vs bulk concentration of cadmium (x_{Cd}) in liquid Cd-Zn alloy at 800K.

Figs. (3) and (4) are respectively the plots of surface concentration and surface tension against bulk concentration of cadmium in liquid Cd-Zn alloys at 800K. It is noticed that surface concentration of cadmium in Cd-Zn alloys is found to be larger than concentration from additive rule; it increases with increase of its bulk concentrations (Fig. 3). Theoretical analysis gives that the computed surface tension for Cd-Zn alloys at 800K is less than ideal values at all concentration of cadmium; i.e. there is negative departure of surface tension from ideality. Two approaches predict that surface tension of Cd-Zn liquid alloy decreases with increase of bulk concentration of zinc (Fig. 4). This is an indication that in the alloys there are more atoms of component with bigger atom at the surface. Hence, at the surface of Cd-Zn, bigger Cd-atoms segregate at the surface in preference to Zn-atoms throughout the entire composition. The segregation of the components may result from the differences surface tension, atom radius and electron configuration between solvent and solute.

CONCLUSIONS

Following conclusions are drawn about liquid Cd-Zn alloys at 800K:

- The alloy is of a weakly interacting nature.
- It is of phase-segregating system.
- Viscosity isotherm of the alloy is found to deviate negatively from ideality.
- Consistency is occurred in the values of surface tension obtained from two approaches, negative departure of surface tension from ideality is observed.
- The surface of liquid Cd-Zn alloys is enormously rich with bigger Cd atoms.

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