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Energetics of mixing and transport phenomena in Cd-X (X=Pb, Sn) melts

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Abstract

We report a quasi-chemical study of the thermodynamic and transport properties of mixing of liquid Cd-Pb and Cd-Sn alloys at 773K. The interaction energy in the alloys is found to be positive which suggests homo-coordination of atoms in the alloys. The viscosities of the alloys at 773K computed from two different approaches exhibit non-linear concentration dependence with the results for Cd-Sn alloy being in very good agreement and satisfactory agreement for Cd-Pb alloy. In lower concentrations of Cd-component, Cd-Pb alloy has larger viscosity and on the other side of concentration, Cd-Sn alloy has larger value. The calculations of inter-diffusion coefficients result in concave diffusion isotherms for the alloys. The higher values of inter-diffusion coefficients for Cd-Sn suggest that Cd and Sn metals tend to mix more readily than Cd and Pb metals do in Cd-Pb alloy. The correlation between viscosity and diffusion implies that the inter-diffusion coefficient is large for low viscous liquid alloy and vice-versa.

Keywords: Mixing properties; Transport properties, Diffusion; Free energy of mixing.

1. Introduction

Of various traditionally classified materials such as metals, semiconductors, alloys, ceramics and polymers in use today, metal alloys make up a large proportion both by quantity and commercial value. The major building materials of the industrial revolution are indeed metals and alloys. Among a vast number of metallic alloys so far produced, those with cadmium metal have received much attention from both experimental and theoretical researchers and in the context two liquid alloys namely Cd-Pb and Cd-Sn in particular have become the subject of various research studies over several decades [1-9]. This is due to interest in these alloys for the substantial variation in their observed properties [10] and wide range electrical, mechanical, coating, and especially high-temperature structural applications [11].

In metallurgical science the determination of the mixing properties of liquid alloys is prerequisite for the preparation of desired materials for commercial use. Growing technological interest to the non-periodicity in the atomic arrangement of liquid alloys has led metallurgists to emphasize understanding of the high temperature dynamics of the alloys in the liquid state for the description of

the behaviour and performance of the commercial alloys in the solid state. The dynamics in fluids is governed by two intimately related transport phenomena namely viscosity and atomic diffusion. The viscosity and diffusion of metals and the alloys are technologically important properties which are required for the interpretation of the kinetics of the reactions and modelling of metallurgical processes. While the first describes the macroscopic transport of momentum by the collective motion of the particles, the latter describes single-particle diffusive transport. The interest for the study of the transport phenomena in liquid alloys thus stems from the significance of these properties in both the technology and theory of the liquid alloys.

As the variation in the elemental composition in the metallic mixture produces alloys with different properties, it is logical to examine the alloying behavior by computing the properties of mixing as function of concentration. In the current work we have focused our attention towards the review of the thermodynamics of the formation of liquid Cd-Pb and Cd-Sn alloys at 773K and the transport phenomena in them. For the review of the thermodynamics of mixing in the liquid alloys as function of composition we employ self-association model based on the formation of like atom clusters [12, 13]. The self-association model is assumed to be good for regular alloys [14], and to our interest we intend to apply it to the alloys, which are not strictly regular solutions but have their behaviour close to that of regular solution. Due to unavailability of reference experimental data of viscosity at hand, we cannot compare the results which can be obtained from a model and for this reason we have carried out a comparative study using quasi-chemical analysis [15] and Moelwyn-Hughes (M-H) equation [12]. In order to study of transport behaviour in the liquid alloys in further detail we have also assessed inter-diffusion coefficients of the alloys from the quasi-chemical approach [16]. The outline of the paper is as follows: Theoretical basis of the work is presented in Section 2. Sections 3 and 4 deal with the results and discussions respectively and conclusions are outlined in section 5.

2. Theoretical basis

2.1 Thermodynamic Properties

Let us assume that a liquid binary alloy contains altogether N atoms, of which N_{c_A} are atoms of element A and N_{c_B} are atoms of element B. In self-association model for regular alloy [5] the atoms of the elements A and B are assumed to be located at equivalent sites with short range interactions effective only between nearest neighbours in polyatomic matrices. This leads to the formation of like atom clusters or self-associates of type iA and jB , where i and j are the numbers of atoms in the clusters of type A and B matrices respectively. On the basis of such assumption, expressions for thermodynamic functions are derived for liquid binary alloys [12, 13].

The free energy of mixing, G_M is obtained using the following analytical expression [12, 13]:

$$G_M = RT [c_A \ln \phi + c_B \ln(1 - \phi)] + \phi(1 - \phi)(c_A + n c_B)W \quad (1)$$

$$\text{with} \quad \phi = \frac{c_A}{c_A + n c_B} \quad (2)$$

Here, R is molar gas constant; T is the temperature; c_A and c_B are concentrations of components A and B respectively; W is ordering energy parameter and $n = j/i$ is the ratio of the self-associates.

In order to estimate the value of the energy parameter W , we also recall the following standard thermodynamic relations for the chemical activities, a_k [12, 13]:

$$\ln a_A = 1 + \ln \phi - \frac{\phi}{c_A} + (1 - \phi)^2 \frac{W}{RT} \quad (3a)$$

$$\ln a_B = \ln(1 - \phi) + \phi(1 - n) + n\phi^2 \frac{W}{RT} \quad (3b)$$

An analytical expression for the entropy of mixing, S_M can be obtained, from Eq. (1), in the following form:

$$S_M = -R [c_A \ln \phi + c_B \ln(1 - \phi)] + \phi(1 - \phi)(c_A + n c_B) \frac{\partial W}{\partial T} \quad (4)$$

The enthalpy of mixing H_M is calculated from the following standard thermodynamic relation:

$$H_M = G_M + T S_M \quad (5)$$

2.2 Transport Properties

2.2.1 Viscosity

Unlike equilibrium properties, for which more or less accurate expressions have been derived on the basis of statistical mechanical theory, the derivation of computable, exact expressions for the dynamic properties of the liquid alloys is a complex task as it is hard to describe atomic motions precisely in the liquid phase. The scientific literature provides a number of semi-empirical equations or approximate expressions for the computation of the viscosity of the metals and the alloys [15, 17-20]. For want of the experimental results for the viscosities of the alloys in this work, we have performed comparative study using the following two different approaches for the computation of viscosities of liquid Cd-Pb and Cd-Sn alloys.

(i) Quasi-chemical approach

The concentration dependence of the viscosity of metal alloy at a given temperature can be computed from the following expression [15]:

$$\eta = (c_A \eta_A + c_B \eta_B) [1 - c_A c_B g(n, W)] \quad (6)$$

where
$$g(n, W) = \frac{2n^2(W/RT) - (n-1)^2(c_A + n c_B)}{(c_A + n c_B)^3} \quad (7)$$

with n and W/RT being the fitting parameters appearing in the self-association model, Eq. (1).

The viscosities, η_k ($k=A, B$) of pure metals can be calculated from the knowledge of their viscosities at their respective melting temperatures using the Iida-Guthrie equation for temperature dependence as follows [20]:

$$\eta_i = \eta_{oi} \exp(2.32 T_{m,i}^{1.29} / RT) \quad (8)$$

With
$$\eta_{oi} = \frac{\eta_{m,i}}{\exp(2.32 T_{m,i}^{1.29} / RT_{m,i})} = \frac{\eta_{m,i}}{\exp(0.279 T_{m,i}^{0.29})} \quad (9)$$

The performance of the equations for the temperature dependences of the above equations have been analysed by computing the results for different metals and comparing with the corresponding experimental results [20, 21].

(ii) Moelwyn-Hughes (M-H) equation

The viscous flow of a liquid mixture depends on the cohesive interactions in liquid phase. Cohesive interactions arise due to the bonding that develops between atoms/or molecules and their nearest neighbours and they give rise to the enthalpic effect. In order to account for viscous flow in a binary liquid mixture, a simple equation, called Moelwyn-Hughes (M-H) equation [12], has been suggested which is based on fact that the viscous flow becomes more difficult when the cohesion energy of the alloy is increased. The M-H equation for the viscosity, η of binary solution at temperature T as function of mole fraction concentration, c_i ($i = A, B$) reads as

$$\eta = (c_A \eta_A + c_B \eta_B) [1 - c_A c_B (2W / RT)], \quad (10)$$

where W is the interaction energy which can be estimated from self-association model, Eq. (1) and η_A and η_B being the viscosities of the components at temperature T .

The sign of deviation of viscosity from linearity depends only on the sign of W . For segregating systems, $W > 0$ and, therefore, $\eta < \eta_{id}$, i.e. negative deviation of viscosity is expected for these systems. For ordering systems on the other hand, $\eta > \eta_{id}$ is expected.

2.2.2 Diffusion

Atomic diffusions in metals and alloys are important transport phenomena in metallurgical science. To study atomic diffusion theoretically, several models/equations have been suggested. An equation for the self diffusivity or intrinsic diffusion coefficients, $D_{m,i}$ of liquid metals at their melting points, $T_{m,i}$ has been derived through a combination of the modified Stokes-Einstein relation and the Andrade formula for melting-point viscosity [22], as well as the hard-sphere model [23] and the corresponding-states principle [22] in the form [24]:

$$D_{m,i} = 1.32 \times 10^{-9} (T_{m,i} / M_i)^{1/2} V_{m,i}^{1/3} \quad (11)$$

where M_i is the atomic mass and $V_{m,i}$ is the atomic volume.

The temperature dependence of self-diffusivity of liquid metals can be expressed by the Arrhenius equation [24] as follows:

$$D_i = D_{o,i} \exp(-E_{D,i} / RT) \quad (12)$$

where the pre-exponential constant, $D_{o,i}$ and the apparent activation energy of self-diffusivity for metal, $E_{D,i}$ are called Arrhenius parameters. The parameter $E_{D,i}$ is related to its melting temperature, $T_{m,i}$ as

$$E_{D,i} = 12.6 T_{m,i}^{1.11} \quad (13)$$

The parameter $D_{o,i}$ is obtained by substituting $T = T_{m,i}$ and $D_i = D_{m,i}$ in Eq. (12)

$$D_{o,i} = D_{m,i} \exp(12.6 T_{m,i}^{0.11} / R) \quad (14)$$

For a binary system of constant molar volume, the inter-diffusion coefficient, D_m can be expressed as follows [16]:

$$D_m = (c_B D_A + c_A D_B) \left(1 + \frac{d \ln \gamma_A}{d \ln c_A} \right) \quad (15)$$

where γ_A is the activity coefficient of A, D_A and D_B are the self-diffusivities of the components A and B respectively. In quasi-chemical analysis a workable expression for the factor $(1 + d \ln \gamma_A / d \ln c_A)$ can be derived from Eq. (3), in terms of the fitting parameters n and W of self-association model in the form

$$1 + \frac{d \ln \gamma_A}{d \ln c_A} = \frac{n}{n + c - nc} + \frac{c(1-n)}{(n + c - nc)^2} + \frac{2n^2 c(c-1)}{(n + c - nc)^3} \frac{W}{RT} \quad (16)$$

Having known the parameters n and W , the inter-diffusion coefficient, D_m of the binary liquid alloys can then be computed.

3. Results

The thermodynamics of mixing in metallic alloys can be regarded as the interplay between enthalpic and entropic effects which gives rise to the nature of nature of alloy, either ordering or segregating. At

a given temperature and fixed pressure, equilibrium mixing properties of a binary liquid alloy vary with the composition of the alloy. To begin with we have fitted the parameters of the self-association model into Eqs. (1-3) separately to be respectively ($n=1.31$, $W/RT=1.212$) and ($n=1.225$, $W/RT=0.545$) for Cd-Pb and Cd-Sn alloys at 773K, so as to reproduce closely the corresponding experimental values of the free energy of mixing, G_M and activities, a_k over the entire range of concentration [10]. We have next computed the entropy of mixing, S_M taking $dW/dT = -2.25$ and -4.45 in Eq. (4) respectively for Cd-Pb and Cd-Sn alloys and then the enthalpy of mixing, H_M for the alloys from Eq. (5). Numerical results of the thermodynamic functions G_M , S_M and H_M along with the corresponding reference values [10] are depicted in the isotherms of Fig.1(a) for Cd-Pb alloy and those for Cd-Sn alloy in Fig. 1(b).

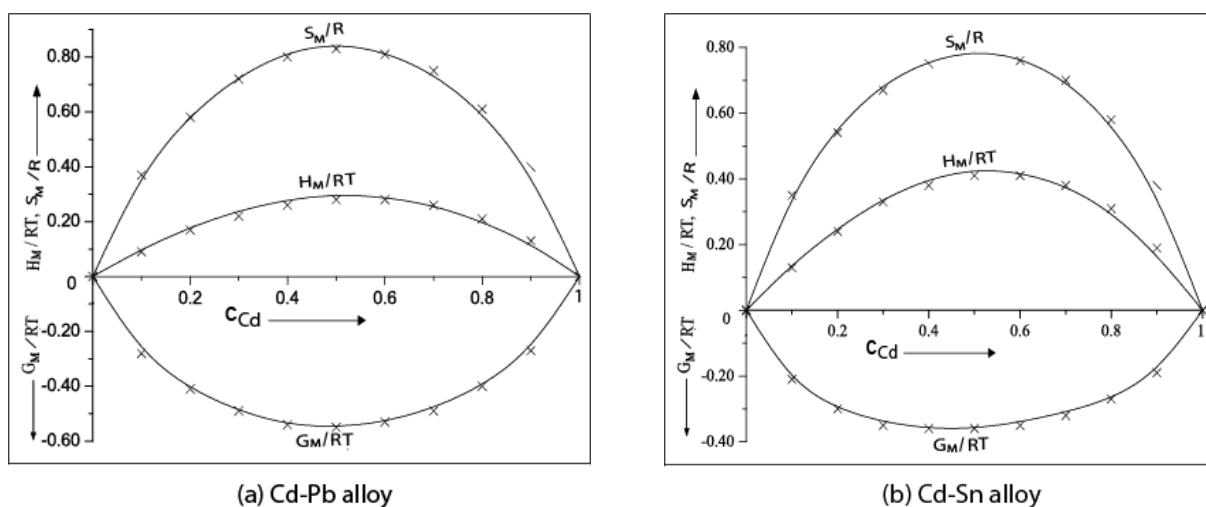


Fig. 1: Thermodynamic functions G_M , S_M and H_M versus concentration of Cd-component of (a) Cd-Pb alloy at 773K and (b) Cd-Sn alloy at 773K [Solid line- Theory; Crosses- Experiment].

The dynamic mixing behaviour of the alloys is studied in terms of the atomic transport coefficients namely viscosity and diffusion coefficients. The knowledge of viscosity helps to understand the bonding strengths among various species in the liquid alloys. For calculations of the viscosity of the alloys, the viscosities of the pure metals Cd, Pb and Sn at the temperature of investigation are required which are calculated from Eq. (8) using the values of their viscosities at the respective melting temperatures [20]. We have then computed the concentration dependence of the viscosity of liquid alloys using separately the values of the interaction energy W as thermodynamic input for each alloy. Due to scanty of reference data of the alloys for comparison, we have carried out comparative analysis by computing the viscosities from the quasi-chemical approach, Eq. (10) over the full range of concentration. The results for viscosity of alloys calculated from M-H equation and quasi-chemical approach are found to be reasonably in good agreement with negative deviation from the additive rule of mixing [Fig. 2 (a)].

In order to examine the dynamic behaviour in the alloys at 773K in some more detail, we have also computed inter-diffusion coefficients as function of concentration using Eq. (15) in conjunction with Eq. (16). The inter-diffusion isotherms for both the alloys are found concave with a minimum value at 60% atomic composition of Cd-content for Cd-Pb alloy and at 50% for Cd-Sn alloy [Fig. 2 (b)]. The higher values of inter-diffusion coefficients for Cd-Sn suggest that Cd and Sn metals tend to mix more readily than Cd and Pb metals do. This is in conformity with smaller segregating tendency in Cd-Sn alloy.

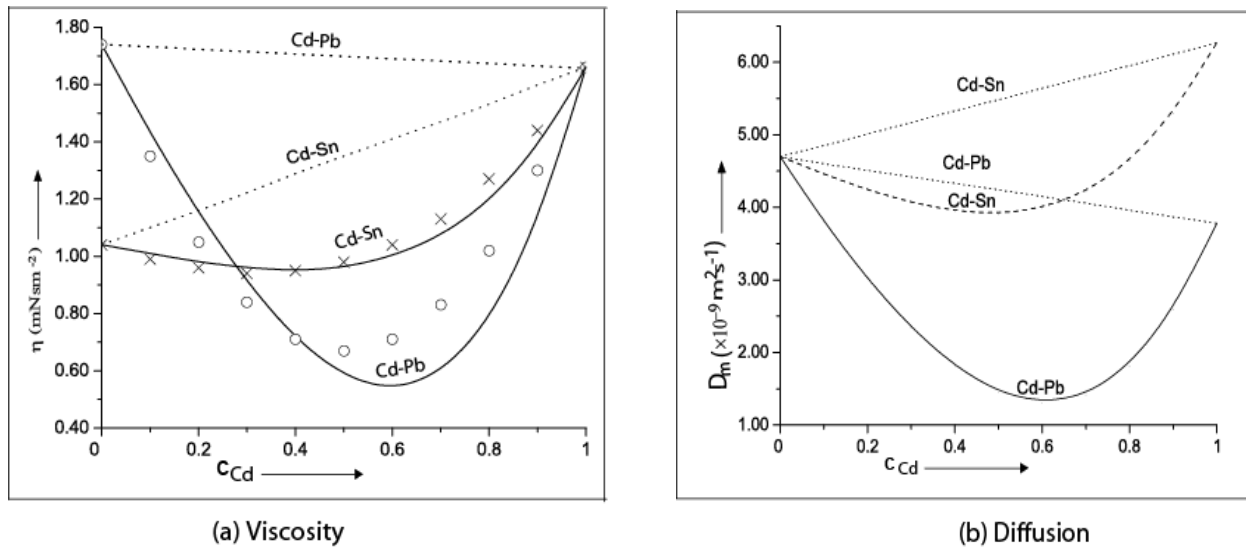


Fig. 2: (a) Viscosity of Cd-Pb and Cd-Sn alloys at 773K versus concentration of Cd-component [Solid curve- Quasi-chemical approach; Circles and crosses- M-H equation; Dots- Ideal values] (b) Inter-diffusion coefficient (D_m) of Cd-Pb and Cd-Sn alloys at 773K [Solid line-Theory; Dots- Ideal values].

4. Discussion

The interaction energy parameters estimated in our study are model specific and the prediction of the properties of the alloys using the energy parameters is a success of the model. The positive sign of the energy parameters in both the alloys suggests a general tendency of repulsive interaction between corresponding species in that results in homo-coordination of the atoms in the alloys showing positive deviation from Raoult's law. For either alloy the temperature derivative of order energy has been found to be a non-zero quantity. This suggests that the interaction energy in an alloy is temperature dependent.

In our comparative study, the viscosities of the alloy are found to have non-linear (concave) concentration dependence with the results from the two approaches for Cd-Sn alloy being in very good agreement and it is also reasonably good enough to accept the departure in the results for Cd-Pb alloy. It is apparent from the viscosity isotherms that Cd-Pb has larger viscosity in lower concentration of Cd-component while Cd-Sn alloy has larger value in Cd-rich side of the composition.

The local atomic ordering in a liquid A-B alloy is non-periodic, unlike crystals, as the solute atoms in the homogeneous solution can arrange in many ways by diffusion which contrasts with the pure metals A and B, in each of which the atoms can arrange only in a particular way. In the state of disorder in the atomic arrangements, some sort of short range atomic bonding (metallic, ionic, or covalent, or even secondary bonds, such as hydrogen bonding or Vander Waals forces as in the case of molecular crystals or liquids) can be assumed to exist between the nearest neighbours to present cohesive energy of solution. The cohesive energy of solution depends on the size difference of the atomic species and entirely to the size-dependent variations in the latent heats [25]. The cohesive energy may be thought to be responsible for the enthalpic effect and the viscous nature of the liquid alloys. In general larger viscosity values of a liquid alloy indicate stronger cohesive interactions in it suggesting a slow viscous flow of the melt.

It is noted that the agreement in the results from different equations for viscosity of alloys casts considerable doubt on the reliability of the results and hence suggests the limitations to the validity of

the equations. Indeed, it is very difficult to judge the reliability of such work without a clearer understanding of the controlling factors involved. At this point it would be proper to mention that the equations, which we have employed in this work for computing viscosities of binary liquid alloys, have already been applied in several other studies.

It is apparent that the mutual diffusion of liquid metals in forming a binary liquid alloy depends on sizes of the atomic species; it is found to be preferably large when the atomic volumes of the component metals are nearly equal and it decreases as the size ratio deviates from unity. It is found to be preferably large when the atomic volumes of the component metals are nearly equal and it decreases as the size ratio deviates from unity. Moreover, it is mentioned that diffusion coefficient varies inversely with viscosity when the ratio of solute to solvent exceeds five and in extremely high viscosity materials, diffusion becomes independent of viscosity [22].

5. Conclusion

Our theoretical analysis of mixing properties of Cd-Pb and Cd-Sn alloys at 773K shows that self-association model successfully explains the observed thermodynamics of mixing in the alloys showing positive deviation from Raoult's law. The analysis of viscosity calculations reveals non-linear concentration dependence of viscosity for both the alloys. In lower concentrations of Cd-component, Cd-Pb alloy has been found to have larger viscosity and on the other side of concentration, Cd-Sn alloy has larger value. The calculations of inter-diffusion coefficients result in concave diffusion isotherms for the alloys. The higher values of inter-diffusion coefficients for Cd-Sn suggest that Cd and Sn metals tend to mix more readily than Cd and Pb metals do in Cd-Pb alloy. The correlation between viscosity and diffusion is remarkable which simply suggests that the diffusion coefficient is large for low viscous liquid alloy and vice-versa.

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