

Mixing properties of X–Pb, (X = Cd, In) liquid binary alloys

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Abstract

We study the mixing properties of Cd–Pb and In–Pb segregating alloy systems using the Quasi-chemical approximation model (QCAM) within the framework of Quasi-lattice theory (QLT). The energetics of mixing in liquid binary alloys has been analyzed through the study of the various thermodynamic quantities. Positive deviation from Raoultian behavior was observed in the mixing properties of the alloys calculated. Our results are in good agreement with reported experimental data and support a weak demixing tendency in both Cd–Pb and In–Pb liquid alloys.

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1. Introduction

Many investigations have been reported in literature on liquid binary alloy systems which are of importance from both the scientific and also the technological points of view. An accurate knowledge of the mixing properties and phase diagrams of the alloy systems are essential to establish a respectable understanding between the experimental results, theoretical approaches and empirical models for liquid alloys with a miscibility gap.

The interatomic interactions and the related energies of the bond between the A and B component atoms of a binary alloy play an essential role in understanding the mixing behavior of two metals. In the light of this, the energetically preferred heterocoordination of A–B atoms as nearest neighbors over self-coordination A–A and B–B, or vice versa lead to the classification of all binary alloys into two distinct groups: short-range ordered [1–5] or segregating (demixing) alloys [6–9].

One notes that cadmium and indium are typical metals in group IIB and IIIB of the periodic table. Compounds and alloys of these groups have been widely used in fabri-

cating solid-state electronic components. Cadmium is used in many types of solder for standard electromotive force cells, for Ni–Cd batteries, and as a barrier to control atomic fission. It is also used in electroplating of automotive, aircraft and in photoelectric cells in fire protection systems. Indium on the other hand is used as a strengthening agent for lead solders and as the base material for many low melting point solders.

It is observed that both systems investigated, Cd–Pb and In–Pb are characterized by a positive interaction energy, indicating the formation of two-phase structures, as shown by their phase diagrams [10]. This characteristic behavior is likely to be a reflection of the interplay of the energetic and structural re-adjustment of the constituent elemental atoms. However, this is discussed in terms of metallurgical and chemical constructs, such as electronegativity difference ($=-0.1$ and -0.1) [11] and size mismatch ($=1.39$ and 1.19) [12] for the Cd–Pb and In–Pb alloys, respectively, which indicate values that are characteristic for segregating alloys [6]; and it can be ascribed to the size mismatch values, $\frac{V_{\text{Pb}}}{V_{\text{Cd}}} \approx 1.39$ and $\frac{V_{\text{Pb}}}{V_{\text{In}}} \approx 1.19$ that suggest a limited solubility in the solid-state [13].

The concentration fluctuations in the long-wavelength limit, $S_{\text{cc}}(0)$, the Warren–Cowley chemical short-range order parameter (CSRO), α_1 , the diffusion coefficient (D),

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the enthalpy of mixing, H_M and the entropy of mixing, S_M of Cd–Pb and In–Pb molten alloys deviate positively from the ideality and thus both alloys belong to the class of liquid alloys that exhibits a preference towards homocoordination (segregation).

In this work, we study the composition dependence of thermodynamic properties of liquid Cd–Pb and In–Pb by the Quasi-chemical approximation model. The energetics of mixing as well as the positive deviation from Raoultian behavior was discussed for the various bulk properties calculated. It is known that for segregating alloys the size effects have an appreciable influence on their surface properties [6]. The degree of these effects increases together with a preference of a system toward phase separation.

The layout of this paper is as follows. In Section 2, we present the theory of Quasi-chemical approximation model (QCAM) for calculating the thermodynamic properties of binary liquid alloys. This is followed by results and discussion in Section 3 and finally, we conclude the paper in Section 4.

2. The theory of QCAM

The general mathematical expression for the grand partition function Ξ of a binary molten alloy AB, which consists 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

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp[(\mu_A N_A + \mu_B N_B - E)/k_B T], \quad (1)$$

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. The Quasi-chemical approximation model is utilized to determine the probable chemical complexes existing in a liquid binary alloy. Detailed discussion of the theory are given in [14].

In order to calculate the bulk thermodynamic properties, the excess Gibbs free energy of mixing G_M^{xs} is related to the free energy of mixing G_M by Eqs. (2)–(6) have been used to compute the interaction parameters, given in Eq. (6)

$$G_M^{xs} = G_M - RT\{c \ln c + (1 - c) \ln(1 - c)\}. \quad (2)$$

The Quasi-chemical expression for the excess free energy of mixing G_M^{xs} is given as

$$\frac{G_M^{xs}}{RT} = z \int_0^c [\ln \sigma + (2k_B T)^{-1} (P_{AA} \Delta \epsilon_{AA} - P_{BB} \Delta \epsilon_{BB})] dx + \phi, \quad (3)$$

where z is the coordination number, c is the concentration of atom A and R is the universal gas constant; and

$$\ln \sigma = \frac{1}{2} \ln \frac{(1 - c)(\beta + 2c - 1)}{c(\beta - 2c + 1)}, \quad (4)$$

with

$$\beta = \{1 + 4c(1 - c)(\eta^2 - 1)\}^{1/2}, \quad (5)$$

where

$$\eta^2 = \exp\left(\frac{2\omega}{zk_B T}\right) \exp\left(\frac{2P_{AB}\Delta\epsilon_{AB} - P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB}}{k_B T}\right), \quad (6)$$

ω , $\Delta\epsilon_{AB}$, $\Delta\epsilon_{AA}$, $\Delta\epsilon_{BB}$ are the interaction parameters with ω denoting the interchange or ordered energy and $\Delta\epsilon_{ij}$ is the change in the energy of the ij bond in the complex $A_\mu B_\nu$. P_{ij} is the probability that the ij bond is a part of the complex in the mixture and can be expressed as follows:

$$P_{AB} = c^{\mu-1}(1 - c)^{\nu-1}[2 - c^{\mu-1}(1 - c)^{\nu-1}], \quad (7)$$

$$P_{AA} = c^{\mu-2}(1 - c)^\nu[2 - c^{\mu-2}(1 - c)^\nu] \quad \mu \geq 2, \quad (8)$$

$$P_{BB} = c^\mu(1 - c)^{\nu-2}[2 - c^\mu(1 - c)^{\nu-2}] \quad \mu \geq 2. \quad (9)$$

The constant ϕ in Eq. (3) is determined from the condition that $G_M = 0$ at $c = 1$.

For simple regular alloys, the Quasi-chemical expression reduces to a one-parameter model and the excess Gibbs free energy of mixing is expressed as [15]

$$G_M^{xs} = RT[c \ln \gamma_A + (1 - c) \ln \gamma_B], \quad (10)$$

where the activity coefficients γ_A and γ_B can be easily obtained by the Fowler–Guggeheim method, as reported in [16,17]:

$$\gamma_A = \left(\frac{\beta - 1 + 2c}{c(\beta + 1)}\right)^{z/2}, \quad (11)$$

$$\gamma_B = \left(\frac{\beta + 1 - 2c}{(1 - c)(\beta + 1)}\right)^{z/2}. \quad (12)$$

with β already defined by Eq. (5). However, for a simple regular alloy, η is given by

$$\eta = \exp\left(\frac{\omega}{zk_B T}\right). \quad (13)$$

The activities of the alloys are obtained by

$$a_i = c\gamma_i. \quad (14)$$

Here, c is the concentration of the species and γ_i are their respective activity coefficients given in Eqs. (11) and (12).

The work of Bhatia and Thornton [18] would enable us to visualize the nature of mixing and the degree of order in the melt in terms of chemical order [19] and segregation [6] by two microscopic quantities. Firstly, the concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, describes the nature of mixing of liquid alloys indicating chemical order and segregation [14] and it is also directly related to transport properties as diffusion [6,8]. The $S_{cc}(0)$ can be expressed by G_M , or the activity, $a_i (i = A, B)$, as

$$\begin{aligned} S_{cc}(0) &= RT \left(\frac{\partial^2 G_M}{\partial c_A^2} \right)_{T,P,N}^{-1} = c_B a_A \left(\frac{\partial a_A}{\partial c_A} \right)_{T,P,N}^{-1} \\ &= c_A a_B \left(\frac{\partial a_B}{\partial (1 - c_A)} \right)_{T,P,N}^{-1}. \end{aligned} \quad (15)$$

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