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Correlation between bulk and surface properties in Rb–Pb liquid alloy

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Abstract

Correlation between bulk thermodynamic properties and surface properties in Rb–Pb liquid alloys has been studied using a statistical model based on compound formation. This study shows that the compound formation in the bulk resulted in an increased surface tension values. A reduced surface concentration of rubidium atoms was also observed. The surface concentration fluctuation at the long wavelength limit $S^{s}_{cc}(0)$ indicates tendency to a regular mixing of alloy components on the surface at high bulk concentrations of Rb.

Keywords: Liquid alloys; Activity; Concentration fluctuation

1. Introduction

The anomalies exhibited in the electrical and thermodynamic properties of alkali–lead liquid alloys have posed interesting challenges to researchers. Some of these unusual behaviors of this class of liquid alloys occur at the octet or around the equiatomic composition [1–4]. In particular, rubidium–lead (Rb–Pb) liquid alloys have been reported to exhibit a large heat capacity anomaly about its equiatomic concentration [2,5]. The electrical resistivity showed a maximum and a large negative temperature coefficient was observed for this alloy about the same equiatomic concentration [6,7]. The work of Tamidajski et al. [5] has also shown the peculiarity in its excess entropy of mixing which showed a V shape with the deep still about the equiatomic concentration.

In general, the structural studies of liquid alkali–Pb alloys at equiatomic composition have shown a first sharp diffraction peak (FSDP) at low wave vectors [4], thus suggesting the presence of polyatomic structural units, specifically tetrahedral Pb_4^{4-} Zintl ions [8,9] or double tetrahedral A_4Pb_4 (where A denote the alkali elements). On the other hand, Hafner [10] found that the alkali–Pb alloys also have a tendency to form the 60° Pb–Pb–Pb bond angles found in tetrahedral. He further found that the liquid alloys have broad distribution in coordination numbers indicating that the liquid does not comprise of well defined Pb_4 tetrahedra. Howe and McGreevy [4] also demonstrated that the Pb atoms have a common tendency to form clusters typically three or four atoms with 60° Pb–Pb–Pb bond angle.

The double tetrahedral structure was suggested to explain the structural anomaly observed at equiatomic composition of the liquid alkali–Pb alloys and perhaps to provide reasons for other observed anomalies in the measured properties of these class of liquid alloys about the same composition. Since these anomalies were observed at only the equiatomic composition especially for the Rb–Pb liquid alloy, it suggests that compounds formed with the double tetrahedral structure are unlikely to be present throughout the other concentration ranges of the liquid alloy. It will therefore be of interest to choose a compound whose structure is likely to exist on a larger range of concentration. In this present work, we wish to choose a slightly different configuration by assuming that a compound of the form Rb_xPb_3 is formed in the alloy. Our choice of a compound of this form is predicated by the fact that in the binary phase diagram of Rb–Pb [11], out of five compounds indicated as possibly being present in the alloy about the melting point, three compounds of the form Rb_x Pb_3 namely $RbPb_3$, Rb_2Pb_3 and Rb_4Pb_3 were mentioned.

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This can suggest that the Pb atoms have higher tendencies for a Pb–Pb–Pb bond. We also quickly note that no compound of the form Rb_4Pb_4 was indicated in this phase diagram. This in a way supports the 60° Pb–Pb–Pb cluster suggested by Howe and McGreevy [4]. In addition, the authors [4] expressed reservations with the existence of some tetrahedral Pb_4^{4-} Zintl ions, as they stated from their results that the Pb atoms seem unlikely to occur in such well defined species. This statement makes room for the existence of other configuration of compounds such as the Rb_xPb_3 which are likely to be present in a wider concentration range. In our present circumstance, the use of such configuration in thermodynamic calculations will reproduce the experimental thermodynamic values better and could give better prediction for the behaviour of the system where experimental data are lacking.

The thermodynamic model based on compound formation due to Singh [12] will be used to compute the bulk thermodynamic properties of the liquid alloy. The statistical formulation of Prasad et al. [13] based on the concept of layered structure near the interface for the determination of surface properties links surface properties to bulk thermodynamic properties for a liquid binary alloy. This formulation determines surface properties from energetics and valuable bulk thermodynamic data such as the activity coefficient. On this premise, it will be possible to study the effect of the observed bulk thermodynamic anomalies on surface properties of the liquid binary alloy thus making it possible to make valuable suggestions and inferences on the surface properties of the liquid alloy.

In the section that follows, we present the formulations and essential equations needed for this calculation. In Section 3, the results of the calculations of the thermodynamic properties are given while in Section 4, results and discussion on surface properties calculated based on the thermodynamic inputs are presented. Our conclusions are outlined in Section 5.

2. Theoretical models

The statistical model based on compound formation uses the idea that the thermodynamic properties of a compound forming A–B alloy can be explained by treating the alloy as pseudo ternary mixture of A atoms, B atoms and $A_\mu B_\nu$ complexes. Details of the formulations are given in Ref. [12].

The thermodynamic properties of interest include the Gibbs free energy of mixing, entropy of mixing and activity of the metal in the liquid alloy. The Gibbs free energy of mixing is obtained from the expression,

$$G_m = G_m^{es} + RT[x\ln x + (1-x)\ln(1-x)] \tag{1}$$

where, x is the concentration of atom A, R is the universal gas constant and G_m^{es} is the excess free energy of mixing and its expression in the compound formation model is given as;

$$\frac{G_m^{es}}{RT} = z\int_0^x [\ln\sigma + (2kT)^{-1}(P_{aa}\Delta\varepsilon_{aa} - P_{bb}\Delta\varepsilon_{bb})]dx + \psi \tag{2}$$

where z is the co-ordination number, k, the Boltzmann constant, and $\Delta\varepsilon_{ij}$ is the change in energy if the i–j bond is in the complex $A_\mu B_\nu$. P_{ij} denotes the probability that the bond is part of the complex. The expressions for P_{ij} and $\ln\sigma$ are already clearly given in literature [12]. The constant ψ is determined from the requirement that $G_m = 0$ at $x = 1$.

The entropy of mixing S_m is obtained from the equation

$$S_m = -(\partial G_m/\partial T)_p \tag{3}$$

and the activities of the metals are obtained from the expression

$$a_m = x\gamma_m \tag{4}$$

where x is the concentration of the species and γ_m is its activity coefficient given by

$$\gamma_m = \left\{\frac{\beta - 1 + 2x}{x(1+\beta)}\right\}^{\frac{1}{2}z} \tag{5}$$

The expression for β is already given in [12] and the detailed expression for entropy of mixing under the compound formation model has been given in [14].

The concentration–concentration fluctuations in the long wavelength limit $S_{cc}(0)$ has been shown [12] to be given by

$$S_{cc}(0) = x(1-x)\left\{1 + \frac{1}{2}z\left(\frac{1}{\beta} - 1\right) + \Omega\right\}^{-1} \tag{6}$$

where Ω is the expression given below:

$$\Omega = \frac{zx(1-x)}{2\beta kT}\Theta \tag{7}$$

and

$$\Theta = [2(1-2x)P'_{ab}\Delta\varepsilon_{ab} + (\beta - 1 + 2x)P'_{aa}\Delta\varepsilon_{aa} - (\beta + 1 - 2x)P'_{bb}\Delta\varepsilon_{bb}] \tag{8}$$

where the prime on P denotes the first derivative with respect to x.

A statistical mechanical model which derives from the concept of a layered structure near the interface was used by Prasad and Singh [15], and Prasad et al. [13] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension ζ by the expression

$$\Xi^s = \exp\left(\frac{-A\zeta}{kT}\right) = \exp\left(\frac{-N^s\zeta\xi}{kT}\right) \tag{9}$$

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

Prasad et al. [13] gave the expression for surface tension of the binary alloys in terms of activity coefficient of the alloy components as

$$\zeta = \zeta_A + \frac{kT}{\xi}\ln\frac{x_A^s}{x_A} - \frac{kT}{\xi}\ln\gamma_A + [p(x_B^s)^2 + q(x_B)^2]\frac{w}{\xi} \tag{10}$$