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# Temperature effect on demixing and surface properties of Sn–Zn liquid alloys

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**Abstract**

Effect of temperature on the demixing tendencies in the bulk and surface of Sn–Zn liquid alloy was studied using some statistical models. In the bulk of the Sn–Zn liquid alloy, the demixing tendencies showed a large reduction as temperature increased from 650 to 875 K. With further increase in temperature, Sn–Zn liquid alloy slowly approaches a liquid alloy of ideal mixture of components. Our calculations also indicate that the surface tension of the alloy decreases with increase in temperature below 0.5 bulk atomic fraction of Zn. However, between 0.5 and 0.85 bulk atomic fraction of Zn, there seem to be no obvious trend.


*Keywords:* Liquid alloys; Surface; Demixing

## 1. Introduction

The search for a lead-free solder with suitable properties has drawn the attention of many researchers in recent years [1–4]. This is because lead and its compounds are known to be toxic to the human body and cause serious environmental problems [5,6]. Consequently, the use of lead in microelectronics is being more and more restricted by legislation [2]. Thus the development of lead-free solders has emerged as one of the important issues in the electronic packaging industries [7].

To replace the commonly used Pb–Sn solder, and for certain applications, the ternary X–Sn–Zn alloys are likely to be promising. The component X can be In, Ag, Sb, Bi and or Cu [8–11]. In addition to the properties such as liquidus temperature, pasty range, wettability, microstructure, mechanical properties as well as reliability of soldered joints, it is clear that other factors of interest to be considered for a good soldering candidate material include interfacial adhesion and surface tension as they play important role in producing acceptable solder joints [12,13].

Interfacial reaction and surface tension of a liquid binary alloy can be dependent on the surface composition of the liquid alloy. Prasad et al. [14] have shown that the surface composition and surface tension of a liquid binary alloy are dependent on the nature of the interaction in the bulk of the liquid alloy. In their statistical formulation, Prasad et al. [14] showed that the surface properties are linked to the bulk interactions through the bulk activity coefficients of the alloy components. Using therefore some available thermodynamic data on Sn–Zn [15–18], we wish to determine the trend of the surface properties of this alloy throughout the concentration range with temperature. This in a way will give a clue of the surface behaviour of this alloy at different temperatures. The study will also provide insight into the sensitivity of demixing tendencies of this alloy to temperature.

Sn–Zn belong to a class of alloys, which show endothermic reactions and exhibit large positive enthalpy of formation. This class of liquid binary alloys has been investigated albeit with a lesser degree of interest [19]. Incidentally, Singh and Sommer [20] has developed a statistical model to study

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the thermodynamic properties of some class of alloys which exhibit some close properties to that of Sn–Zn. We first show that this statistical model can describe the thermodynamic properties of Sn–Zn reasonably. This is achieved by using this model to reproduce simultaneously and to a reasonable extent the experimental activity values and Gibbs free energy of mixing at each temperature of investigation. The resulting energetics from these calculations are employed in computing the bulk concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$ and the surface properties at the experimental temperatures.

In the section that follows, the essential equations of the statistical models used for our calculations are highlighted. In Section 3, the results of our calculations are presented and discussed. Conclusions are given in Section 4.

## 2. Theoretical outlines

A simple statistical model proposed by Singh and Sommer [20] for studying the phase separating liquid binary alloys assumes that a liquid binary A–B alloy consisting of $N_A$ atoms of element A and $N_B$ atoms of element B situated at equivalent sites, having short ranged interaction effective only between nearest neighbours forms a polyatomic matrix leading to the formation of like atom clusters or self-associates of type $\mu$A and $\nu$B, where $\mu$ and $\nu$ are the number of atoms in the clusters of type A and B matrices, respectively.

The thermodynamic properties of this category of liquid alloys depends on the number of self-associates, $n = \mu/\nu$, $\mu > \nu$. Using the quasi-chemical approximation, an expression for the Gibbs free energy is obtained as,

$$G_m = RT[c\ln c + (1-c)\ln(1-c) + c\ln(1-\xi) + \ln \Gamma] + c(1-c)\Gamma W \quad (1)$$

where $c$ is the concentration of atom A, $W = \mu w$, $\xi = 1 - 1/n$, $\Gamma = 1/(1-c\xi)$ and $w$ is the interchange energy. The expressions for activity ($a_i$) of the alloy components are given as derived in [20]

$$\ln a_A = \ln(c\Gamma(1-\xi)) + (1-c)\Gamma\xi + (1-c)^2\Gamma^2\frac{W}{RT} \quad (2)$$

$$\ln a_B = \ln(c\Gamma) + c(1-\xi)\Gamma(1-n) + nc^2(1-\xi)\Gamma^2\frac{W}{RT} \quad (3)$$

where $R$ is the molar gas constant and the activity coefficients ($\gamma_i$) can be obtained from the relation $\gamma_i = a_i/c_i$.

Under the present formulation, the $S_{cc}(0)$ is given by the expression

$$S_{cc}(0) = \frac{c(1-c)}{1 - c(1-c)g(n, W)} \quad (4)$$

where

$$g(n, W) = \frac{2n^2(W/RT) - (n-1)^2[c + n(1-c)]}{[c + n(1-c)]^3} \quad (5)$$

Prasad et al. [14] gave the expression for surface tension of the binary alloys in terms of activity coefficient of the alloy components as

$$\sigma = \sigma_A + \frac{kT}{\alpha}\ln\frac{c_A^s}{c_A} - \frac{kT}{\alpha}\ln\gamma_A + [p(c_B^s)^2 + q(c_B)^2]\frac{w}{\alpha} \quad (6)$$

$$\sigma = \sigma_B + \frac{kT}{\alpha}\ln\frac{c_B^s}{c_B} - \frac{kT}{\alpha}\ln\gamma_B + [p(c_A^s)^2 + q(c_A)^2]\frac{w}{\alpha} \quad (7)$$

where $\sigma_A$ and $\sigma_B$ are surface tension values for the pure components A and B, respectively; $c_i$ and $c_i^s$ are the bulk and surface concentrations of the alloy components, respectively; $\gamma_A$ and $\gamma_B$ are the bulk activity coefficients of the alloy components and $w$ the interchange energy.

The surface $S_{cc}(0)$ can be written as [21]

$$S_{cc}^s(0) = c_A^s c_B^s\left[1 + \left(\frac{z^s}{2\beta^s}\right)(1-\beta^s)\right]^{-1} \quad (8)$$

where

$$\beta^s = \left\{1 + 4c_A^s c_B^s\left[\exp\left(\frac{2w}{z^s kT}\right) - 1\right]\right\}^{1/2} \quad (9)$$

Here, $z^s$ is the coordination number of the surface atoms which is obtained from $z^s = (p+q)z$ and $z$ is the coordination number in the bulk.

## 3. Results and discussions

The model proposed by Singh and Sommer [20] was first used to investigate the concentration dependence of some thermodynamic quantities of the Sn–Zn alloys at different temperatures. Firstly, the values of $n$ and $W/RT$ were determined by obtaining a simultaneous overall fit of the experimental activity and Gibbs free energy of mixing($G_m$) at different temperatures of investigation. The values of $n$ and $W/RT$ obtained at different temperatures are given in Table 1. These values are now used to determine the concentration fluctuation at the long wavelength limit $S_{cc}(0)$. These calculated $S_{cc}(0)$ will be used to assess the response of demixing tendencies in the alloy at different temperatures.

Table 1
Model parameters for Sn–Zn liquid alloy

| $T$ (K) | $n$ | $W/RT$ |
|---|---|---|
| 650 | 1.42 | 1.13 |
| 875 | 1.42 | 0.47 |
| 1123 | 1.42 | 0.26 |