Concentration Fluctuation in Long Wavelength Limit in Liquid Magnesium Alloy

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Abstract

The microscopic structure of MgSn liquid alloy at 1073K has been studied by using regular associated solution model. For this we have calculated the concentration fluctuation in long wave length limit $[S_{CC}(0)]$ and chemical short range order parameter (α_1) of liquid MgSn alloy at 1073 K .

Keywords: Binary Alloy; Complex; Chemical order, Microscopic Function

1. Introduction

Liquid alloys, which are disordered systems in the sense of having no long-range atomic or magnetic order, display a remarkable variety of local chemical order. Determination of short range order for alloys has been the subjects of active research for many years. Concentration fluctuation in long wave length limit $[S_{CC}(0)]$ and chemical short range order parameter (α_1) have emerged as powerful microscopic functions [1-8] to visualize the nature of chemical order in the alloy. The phenomena of segregation and compound formation are interpreted through the study of $S_{cc}(0)$ and α_1.

In this paper, we have determined the concentration fluctuation in long wave length limit $[S_{CC}(0)]$ and chemical short range order parameter (α_1) of liquid MgSn alloy at 1073 K using regular associated solution model. In regular associated solution model, it is assumed that strong associations among the constituent species exist in the liquid phase close to the melting temperature. These associations are given different names such as 'complexes', 'pseudomolecules', 'clusters', 'associations' etc. This assumption has been used by several researchers [9-17] to explain the asymmetry of the properties of mixing for binary alloys.

2. Theory

Let the binary alloy AB (=MgSn) consists of n_1 atoms of species A and n_2 atoms of species B. Following Lele and Ramchandrarao [18], it is assumed that chemical complexes ApB ($A_pB <=> Ap+B$) exist in the melt, where p is small integer which is usually determined from the compound –forming concentration (= p / (p+1)) in the solid state. Because of the existence of the compound, liquid alloys are supposed to be composed of three species, namely, monomers A (=Mg), B (=Sn) and complex ApB (=Mg_2Sn) in equilibrium. Let the concentration of A, B and ApB species be n_A, n_B, and n_{ApB} moles respectively. In the partially associated solution the formation of n_{ApB} complex requires $n_1 = n_A + p_{ApB}$ and $n_2 = n_B + n_{ApB}$ for conservation of mass. When there is association, the thermodynamic behaviour of complexes A and B components is governed by their true mole fractions x_A , x_B and x_{ApB} (where $x_A = \dfrac{n_A}{n_A + n_B + n_{ApB}}$ etc.) rather than their gross mole fraction x_1 and x_2, (where $x_1 = \dfrac{n_1}{n_1 + n_2}$ etc.).

Following Lele and Ramchandrarao [18] for the reaction $A_pB \iff pA + B$ the equilibrium constant (k) and the integral excess free energy of mixing (ΔG^{xs}) are given by

$$\ln k = \ln\left(\frac{x_A^p \, x_B}{x_{ApB}}\right) + \frac{\omega_{12}}{RT}[p x_B(1-x_B) + x_A] + \frac{\omega_{13}}{RT}[p x_{ApB}(1-x_A) - x_A] + \frac{\omega_{23}}{RT}[x_{ApB}(1-p x_B) - x_B]$$

$$\text{.............. (1)}$$

and

$$\Delta G^{xs} = \frac{1}{(1 + p x_{ApB})}(x_A x_B \omega_{12} + x_A x_{ApB} \omega_{13} + x_B x_{ApB} \omega_{23}) + \frac{RT}{(1 + p x_{ApB})} \times$$

$$(x_A \ln x_A + x_B \ln x_B + x_{ApB} \ln x_{ApB}) - RT(x_1 \ln x_1 + x_2 \ln x_2) + \frac{x_{ApB}}{(1 + p x_{ApB})} RT \ln k$$

$$\text{........... (2)}$$

Once the expressions for $\Delta G \, [= \Delta G^{xs} + RT(x_1 \ln x_1 + x_2 \ln x_2)]$ is obtained, the concentration fluctuations in the long-wavelength

limit ($S\neg cc(0)$) is related to   through standard thermodynamic relations

$$S_{CC}(0) = RT\,(\partial^2 \Delta G/\partial C^2)_{T,P}^{-1} \quad \ldots\ldots\ldots (3)$$

where C (=) is concentration of A component in the alloy Following D. Adhikari et al. [4], the ($S\neg cc(0)$) is given by

$$S_{CC}(0) = \left\{ \frac{1}{(1+px_{ApB})}\left[\frac{2}{RT}(x_A' x_B' \omega_{12} + x_A' x_{ApB}' \omega_{13} + x_B' x_{ApB}' \omega_{23}) + \left(\frac{x_A'^2}{x_A} + \frac{x_B'^2}{x_B} + \frac{x_{ApB}'^2}{x_{ApB}} \right) \right] \right\}^{-1}$$

$$\ldots\ldots\ldots\ldots (4)$$

where prime denotes the differentiations with respect to concentration and   and   are determined by using relations

$$x_A = x_1 - px_2 x_{ApB}, \quad x_B = x_2 - (1 - px_2)x_{ApB}, \quad x_{ApB}' \text{ is}$$

determined using Equation (1) and the condition $\dfrac{d\ln k}{dC} = 0$.

Experimental values of $SCC(0)$ are directly calculated from the activity data [19] using the following Eqs. [20]:

$$S_{CC}(0) = (1-C)a_1(\partial a_1/\partial C)_{T,P}^{-1}$$
$$= Ca_2(\partial a_2/\partial(1-C))_{T,P}^{-1} \quad \ldots\ldots\ldots\ldots (5)$$

where a_1 and a_2 are the activities of Mg and Sn components respectively.

The chemical short range order parameter (α_1) can be determined from the knowledge of $S_{CC}(0$ [2, 21]. The $-_1$ is given by

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}, \qquad S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)} \quad \ldots\ldots\ldots\ldots (6)$$

where Z is coordination number and its value is taken 10 for our calculation. We note that varying the value of Z does not have any effect on the position of the minima of $á_1$; the effect is to vary the depth while the overall feature remains unchanged.

3. Results and Discussion

We used Eq. (4) to calculate the concentration fluctuation in long wavelength limit Scc(0). For this we need mole fraction of the complex (x_{Mg_2Sn}) and pairwise interaction energies parameters (

ω_{ij}). These parameters were taken from the reference [18]. Figure 1 shows the computed and experimental values of Scc(0) as well as ideal values. The calculated values for Scc(0) shows reasonable agreement with the experimental values. Scc(0) can be used to understand the nature of atomic order in the binary liquid alloys [22,23].
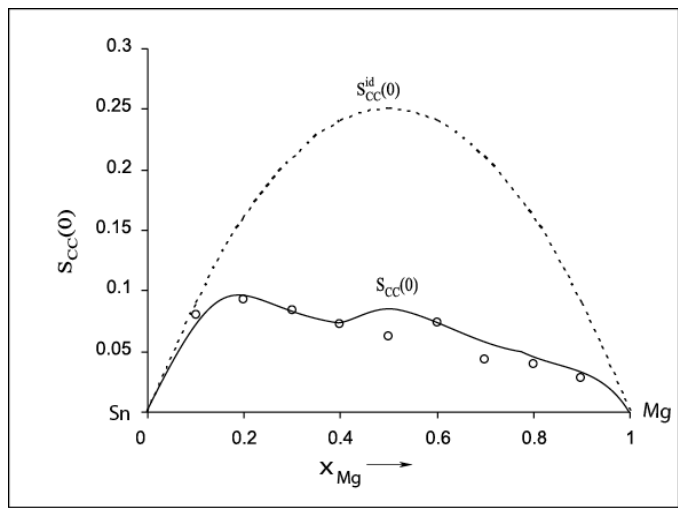

Fig. 1 : Concentration fluctuations in long wavelength limit ($S_{cc}(0)$) versus x_{Mg} of liquid MgSn solution (1073K) ; (——) theory, (○○○) experiment, (----) ideal values.

The condition for occurring order in liquid alloy is Scc(0) $< S_{CC}^{id}(0)$, and if Scc(0) $> S_{CC}^{id}(0)$, there is tendency of segregation. Our theoretical analysis shows that the order exists for MgSn alloy in the liquid state at whole concentration range. We have found that the deviation of Scc(0) from the ideal value is maximum (= 0.168) at $x_{Mg} = 0.61$

The knowledge of α_1 provides an immediate insight into the nature of the local arrangements of atoms in the mixture. At equiatomic composition, one has $-1 \le \alpha_1 \le 1$. The minimum possible value of $á_1$ is -1 and that implies complete ordering of unlike atoms paring at nearest neighbours. On the other hand the maximum value of $á_1$ is +1 which implies total segregation leading to the phase separation and $\alpha_1 = 0$ corresponds to a random distribution of atoms. Figure 2 shows that α_1 are negative throughout, showing MgSn is ordering system of unlike atoms paring at all compositions. The asymmetry in α_1 is distinctly noticeable.
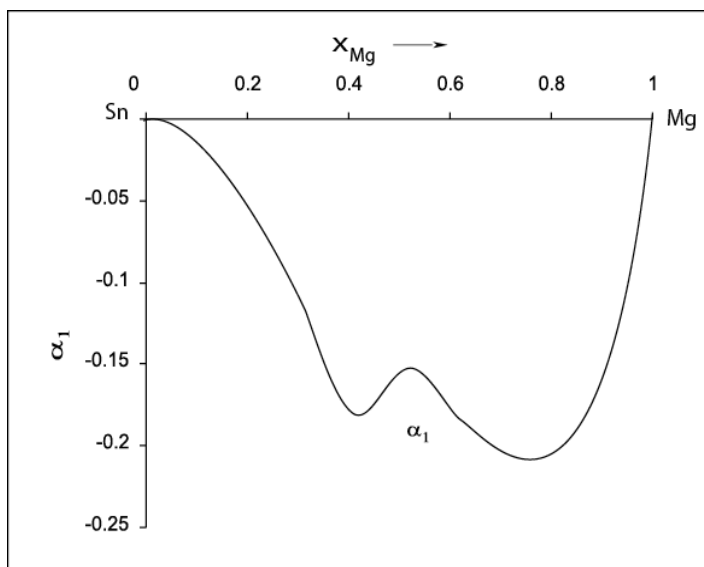
Fig. 2 : *Short range ordering parameter (α_1) of liquid MgSn solution (1073K) versus x_{Mg}.*

4. Conclusion

Computed results of concentration-fluctuation in long wavelength limit and chemical short range order parameter suggest that there is a tendency of unlike atoms pairing (Mg-Sn) in MgSn alloys at all concentration.

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