

# Transport and surface properties of molten Al-Mn alloy

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Received: 16 March 2012, Revised: 08 April 2012 and Accepted: 11 April 2012

## ABSTRACT

The concentration fluctuation in long wavelength limit ( $S_{CC}(0)$ ) has been computed from experimental data of chemical activity of pure Al and Mn components in molten Al-Mn alloys at 1600K. The  $S_{CC}(0)$  is used to obtain Warren-Cowley short range order parameter ( $\alpha_1$ ) and ratio of mutual and intrinsic diffusion coefficients ( $D_M/D_{id}$ ) for this alloy. The surface concentration of pure components with respect to corresponding bulk concentration of pure components for Al-Mn alloy at 1600K has been computed on the basis of Butler's approach. These surface concentrations are then used to calculate the surface tension for this system. Copyright © 2012 VBRI press.

**Keywords:** Surface concentration; bulk concentration; surface tension; geometrical factor.



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## Introduction

Understanding microscopic properties and correlating it with properties of materials form the foundation for studying the process of formation of materials. The functions such as, concentration fluctuation in long wavelength limit, Warren-Cowley short range order parameters are very useful in obtaining the microscopic information on the structure of molten alloys. These functions provide enormous amount of information for understanding metallurgical process and material preparation. The compound formation and phase separation behaviour of molten alloys may be explained in terms of these microscopic functions. The nature of the transition

from the fluid phase to the glassy state can also be explained on the basis of these microscopic functions.

The surface tension of liquid alloys is also an essential parameter for understanding the fundamental theories of metallurgical processes. Several metallurgical phenomena such as, crystal growth, welding, gas absorption, nucleation of gas bubbles are closely associated with the surface tension phenomena. The surface tension is very sensitive to physical and chemical contamination, particularly at high temperatures. But the experimental determination of surface tension involves several difficulties in many cases. Due to this reason, several models [1-4] have long been developed to determine surface tension data of metals and alloys. The purpose of the present work is to compute the microscopic functions for molten Al-Mn alloy using experimental data of chemical activity. The motivation of the study of Al-Mn alloys is Al- alloys are widely used for architectural applications, cooking utensils, chemical equipment, pressure vessels, and heat exchangers. Further we will predict the concentration dependence of surface tension of liquid Al-Mn alloy at 1600 K on the basis of standard model (Butler's model) [4] using the experimental data of different parameters.

Theoretical formalism is given in section 2, section 3 deals with the numerical result and discussion. Conclusion is provided in section 4.

## Theory

### Microscopic functions

The concentration fluctuation in long wavelength limit ( $S_{CC}(0)$ ) is an important microscopic function which is used to understand the ordering and segregating behaviour of binary liquid alloys. The  $S_{CC}(0)$  can be directly related to the experimental activity of each component using standard relations

$$S_{CC}(0) = x_2^b \left( \frac{\partial \ln a_1}{\partial x_1^b} \right)_{P,T}^{-1} = x_1^b \left( \frac{\partial \ln a_2}{\partial x_2^b} \right)_{P,T}^{-1} \quad (1)$$

where  $a_1$  and  $a_2$  are experimental activity of component 1 and that of component 2.  $x_1^b$  and  $x_2^b$  are mole fractions of component 1 and that of component 2 in the bulk. For ideal mixing the  $S_{CC}(0)$  is given by

$$S_{CC}^{id}(0) = x_1^b x_2^b \quad (2)$$

The Warren-Cowley short range order parameter ( $\alpha_1$ ) [5,6] and  $S_{CC}(0)$  are connected to each other by the relation [7,8]

$$\alpha_1 = \frac{S-1}{S(Z)+1} \quad \text{with } S = \frac{S_{CC}(0)}{S_{CC}^{id}} \quad (3)$$

where  $Z$  is coordination number and  $Z=10$  is taken for our calculation. We note that varying the value of  $Z$  does not have any effect on the position of the minima of  $\alpha_1$ ; the effect is to vary the depth while the overall feature remains unchanged. The knowledge of  $\alpha_1$  is very useful to provide

an immediate insight into the nature of the local arrangements of atoms in the mixture.

### Diffusion coefficients

The mixing behaviour of the alloys forming molten metals can also be studied at the microscopic level in terms of the coefficients of diffusion. Singh and Sommer [9] have derived a relation between diffusion coefficients in terms of the  $S_{CC}(0)$  as

$$\frac{D_M}{D_{id}} = \frac{x_1^b x_2^b}{S_{CC}(0)} \quad (4)$$

where  $D_M$  is the chemical or mutual diffusion coefficient and  $D_{id}$  is the intrinsic diffusion coefficient for an ideal mixture given as,

$$D_M = D_{id} \frac{\partial \ln a_1}{\partial x_1^b} \quad (5)$$

with

$$D_M = x_2^b D_1 + x_1^b D_2 \quad (6)$$

where  $D_1$  and  $D_2$  are the self-diffusion coefficients of pure components 1 and 2 respectively.  $D_M/D_{id}$  indicates the mixing behaviour of alloy, i.e.,  $D_M/D_{id} > 1$  indicates the tendency for compound formation and  $D_M/D_{id} < 1$  indicates phase separation. For ideal mixing,  $D_M/D_{id}$  approaches 1.

### Surface properties

Using the condition of equilibrium between the bulk and the hypothetical surface in Butler's approach [4], the surface tension of a liquid solution can be written as

$$\Gamma = \frac{\mu_1^s - \mu_1^b}{A_1} = \frac{\mu_2^s - \mu_2^b}{A_2} = \dots = \frac{\mu_i^s - \mu_i^b}{A_i} \quad (7)$$

where  $\Gamma$ ,  $\mu_i^s$ ,  $\mu_i^b$ , and  $A_i$  denote the surface tension of the solution, the chemical potential of component  $i$  in the hypothetical surface, and that in the bulk, and the molar surface area of pure component  $i$  respectively. The variation of the chemical potential with the composition of the surface layer in ideal solution can be expressed by the same equation in the surface and in the bulk as follows [10]

$$\mu_i^s = \mu_i^{s0} + RT \ln x_i^s, \quad \mu_i^b = \mu_i^{b0} + RT \ln x_i^b \quad (8)$$

where  $x_i^s$  and  $x_i^b$  are mole fraction of component  $i$  in the surface, and that in the bulk.  $R$  is the universal gas constant and  $T$  stands for absolute temperature. It may be proper to mention that  $x_1^b + x_2^b = x_1^s + x_2^s = 1$  for binary mixture. For real solution the mole fractions are replaced by the corresponding activities because the activity coefficients may be different from unity. Now replacing mole fractions by corresponding activities in Eq. (8) and rewriting this equation in terms of partial excess free energy of mixing the surface tension of the liquid solution can be expressed [10, 11]. For binary liquid solution with components 1 and

2 one can express the surface tension using Eqs. (7) and (8) as

$$\Gamma = \Gamma_1 + \frac{1}{A_1}(G_1^{E,s} - G_1^{E,b}) + \frac{RT}{A_1}[\ln(1-x_1^s) - \ln(1-x_1^b)] = \Gamma_2 + \frac{1}{A_2}(G_2^{E,s} - G_2^{E,b}) + \frac{RT}{A_2}[\ln(x_2^s) - \ln(x_2^b)] \quad (9)$$

where  $\Gamma_1$  and  $\Gamma_2$  are surface tension of pure component 1 and 2 respectively.  $G_i^{E,s}$  and  $G_i^{E,b}$  ( $i = 1,2$ ) are partial excess free energy of component  $i$  in the surface and in the bulk respectively.

The molar surface area of the component  $i$  can be computed by the relation [10-13]-

$$A_i = k \cdot N_A^{1/3} \cdot V_i^{2/3} \quad (10)$$

where  $k$  ( $=1.091$ ) is geometrical factor for the liquid alloy [13],  $N_A$  is Avogadro's constant and  $V_i$  stands for the molar volume of the component  $i$ . The molar volume can be calculated from the atomic mass and density of the pure component.

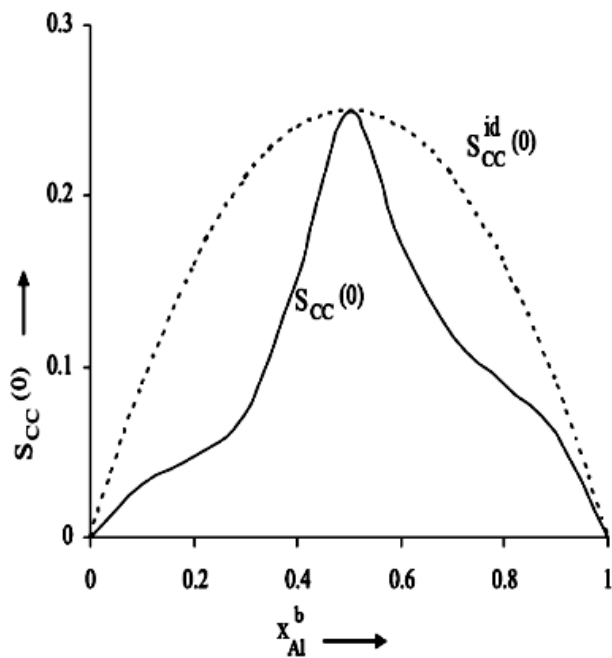


Fig. 1. The concentration fluctuation in long wavelength limit ( $S_{CC}(0)$ ) versus bulk concentration of Al in molten Al-Mn alloy at 1600 K; solid line for  $S_{CC}(0)$  calculated from experimental activity, broken line for ideal value.

## Results and discussion

The concentration fluctuation in long wavelength limit for liquid Al-Mn alloys at 1600K has been computed using Eq. (1). For the computation we need activity data of pure components Al and Mn at the temperature of investigation. We have taken the experimental data of chemical activity from the ref.14. The  $S_{CC}(0)$  calculated from experimental chemical activity is compared with ideal value in Fig. 1. This comparison provides an idea about the ordering and segregating nature of binary mixture [15-19]. If  $S_{CC}(0) < S_{CC}^{id}(0)$ , ordering in liquid alloy is expected and if  $S_{CC}(0) >$

$S_{CC}^{id}(0)$ , there is tendency of segregation. The  $S_{CC}(0)$  computed directly from experimental activity data is found to be less than the ideal value at all composition of Al and Mn in Al-Mn alloys. This means ordering tendency of Al and Mn atoms is preferred in Al-Mn alloys at 1600K in molten state.

In order obtain the better insight in the compound forming nature we have calculated Warren-Cowley short range order parameter ( $\alpha_1$ ) using Eq. (3). The normalized value of  $\alpha_1$  varies from -1 to +1.  $\alpha_1 = -1$  implies complete ordering of unlike atoms paring at nearest neighbours,  $\alpha_1 = +1$  implies total segregation leading to the phase separation and  $\alpha_1 = 0$  corresponds to a random distribution of atoms. We have found the  $\alpha_1$  is negative at all bulk concentration of Al for Al-Mn alloy which is indicative of ordering nature of the alloy as evident from the  $S_{CC}(0)$ . The  $S_{CC}(0)$  are used in Eq. 4. to evaluate the ratio of the mutual and intrinsic-diffusion coefficients,  $D_M/D_{id}$ .

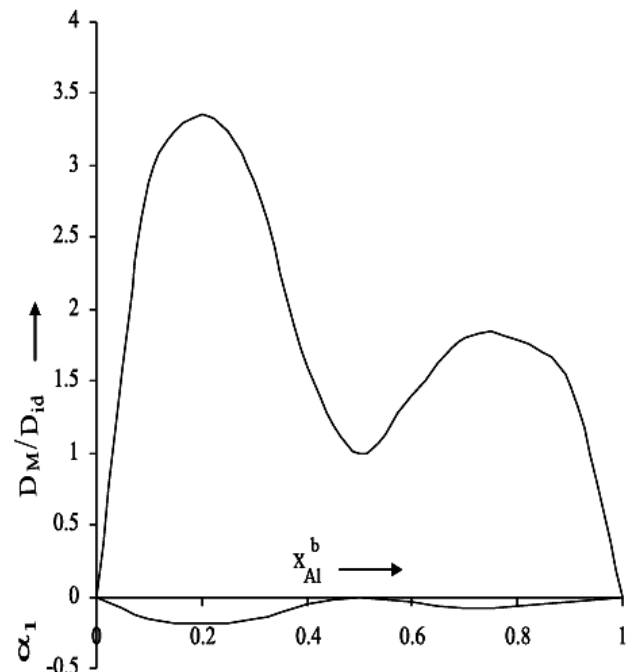


Fig. 2. The ratio of mutual and intrinsic diffusion coefficients ( $D_M/D_{id}$ ) and Warren-Cowley short range order parameter ( $\alpha_1$ ) versus bulk concentration of Al in molten Al-Mn alloy at 1600 K.

The value of  $D_M/D_{id}$  is greater than 1 in the entire range of concentration (Fig. 2) which is indicative for the presence of chemical order in the alloy. The analysis indicates that the ordering tendency of the atoms in Al-Mn alloy in molten state is greater in lower concentration of Al in the bulk. At intermediate region, the ordering tendency of the constituent atoms is weaker as compared to other regions.

The surface tension of a liquid solution can be computed using Eq. (9) if the ratio of partial excess free energy in the surface and that in the bulk is known because all other quantities are either known or can be calculated using available data for pure component. Assuming the partial excess Gibbs energy in the bulk and that in the

surface have the same concentration dependence, their ratio can be expressed as-

$$\beta = \frac{G_i^{E,s}}{G_i^{E,b}} \quad (11)$$

The value of parameter  $\beta$  has been taken different by different researchers to compute the surface tension of liquid metallic solution [20-22]. Yeum et al. [23] calculated  $G_i^{E,s}$  using the quasi-chemical model by Fowler and Guggenheim [24]. Tanaka et al. have suggested the value of this parameter as 0.83 after studying the influence of this parameter taking value from 0.5 to 1 on different systems [25]. Their suggestion for the value of  $\beta$  is also based on the analysis of the dependency of the surface tension of pure liquid metals on their enthalpy of evaporation ( $\Delta H_i$ ) and application to the Cu-Pb and Fe-Si systems. Several researchers [11, 24, 25] have successfully explained the surface tension of different systems (Sn-Ag, Sn-Cu, Pb-Sn) using the values  $\beta = 0.83$  as suggested by Tanaka et al. [25]. Therefore we have also used  $\beta = 0.83$  for the computation of surface tension of Al-Mn alloy in molten state. We have taken the density, surface tension and temperature coefficients for pure Al and Mn components from the ref. 26. The density and surface tension of the pure components at the temperature of investigation have been calculated using the relations

$$\rho(T) = \rho_m + \frac{\partial \rho}{\partial T}(T - T_m) \quad (12)$$

$$\Gamma(T) = \Gamma_m + \frac{\partial \Gamma}{\partial T}(T - T_m) \quad (13)$$

where  $\frac{\partial \rho}{\partial T}$  ( $= -0.28 \text{ Kg m}^{-3}\text{K}^{-1}$  for Al and  $0.70 \text{ Kg m}^{-3}\text{K}^{-1}$ ),

$\frac{\partial \Gamma}{\partial T}$  ( $= -0.15 \text{ mNm}^{-1}\text{K}^{-1}$  for Al,  $-0.20 \text{ mNm}^{-1}\text{K}^{-1}$  for Mn),  $T$  ( $=1600\text{K}$ ),  $T_m$  ( $= 933\text{K}$  for Al and  $1519\text{K}$  for Mn) are temperature coefficient of density, temperature coefficient of surface tension, temperature of investigation and melting temperature respectively.

The partial excess free energies of mixing of the pure components for the systems Al-Mn at 1600 K are taken from the ref. 14. The surface concentration of a component with respect to the bulk concentration has been computed using Eq. (9). The plot (Fig. 3) of surface concentration with respect to bulk concentration shows the positive departure of the surface concentration of Al atoms with respect to the bulk concentration of Al atoms. Due to the differences in the values of surface tension of constituents, the components of the alloy does not get completely mixed with each other in the bulk. Butler's approach enables to find the surface concentration of the component with respect to its bulk concentration.

The analysis implies that there is no complete segregation of Al atoms to the surface. The concentration of Al atoms is greater than Mn atoms in the surface in the region  $x_{Al}^b > 0.3$ . Below this concentration, more Mn atoms

are present in the surface than Al atoms. It indicates that the element with lower surface tension tends to segregate on the surface of molten alloy while the element with higher surface tension tends to segregate inside molten alloy. When there is a larger difference in surface tension between the solvent and solute, the segregating behaviour of the component is more significant.

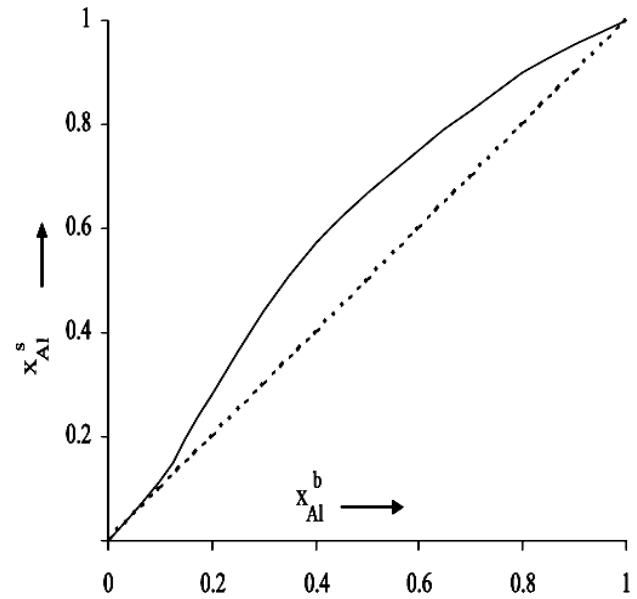


Fig. 3. The surface concentration of Al versus bulk concentration of Al in molten Al-Mn alloy at 1600 K.

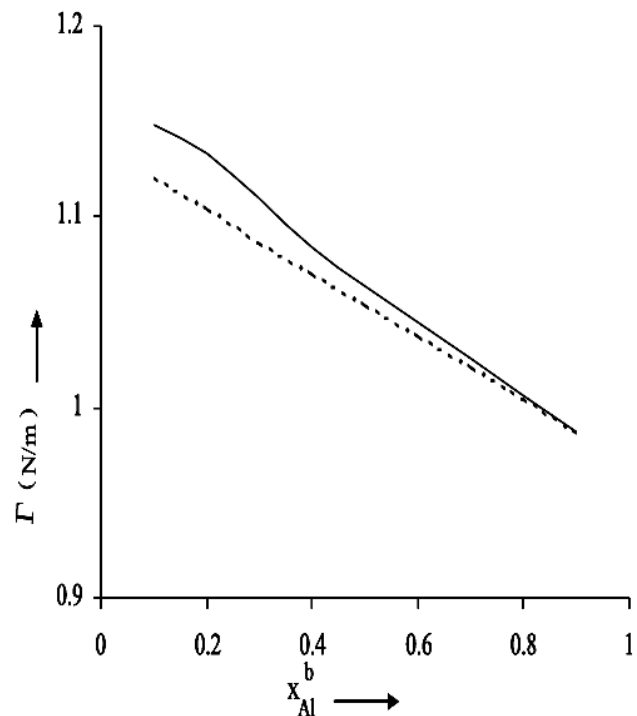


Fig. 4. The surface tension ( $\Gamma$ ) of Al-Mn alloy at 1600K versus bulk concentration of Al in molten Al-Mn alloy at 1600 K; solid line for computed value and broken line for ideal value.



The computed values of surface tension for molten Al-Mn alloy at 1600K are depicted in **Fig. 4**. We do not have experimental values to compare with our computed values of surface tension. However, it is mentioned that the model which we have used in present work has been successfully used by several workers to compute the surface tension of metallic solutions [10, 11]. It is found from the analysis that the computed surface tension for Al-Mn system at 1600K is less than ideal value ( $= x_1\Gamma_1 + x_2\Gamma_2$ ) at all compositions; i.e. there is negative departure of surface tension from ideality. It is also found that the surface tension of this alloy decreases with increase in the concentration of Al component.

## Conclusion

The analysis reveals that there is a tendency of unlike atoms pairing (Al-Mn) in molten Al-Mn alloys at 1600 K in entire range of concentration. The element with lower surface tension tends to segregate on the surface of molten alloy while the element with higher surface tension tends to segregate inside molten alloy. There is positive deviation in the computed value of surface tension from ideality in Al-Mn system at 1600K. The surface tension decreases with increase in the concentration of Al component.

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