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THE ROLE OF SIZE EFFECTS ON SURFACE PROPERTIES

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A theoretical model based on the grand partition function has been developed to investigate the role of size effects on surface tension and surface segregation of liquid binary alloys. The necessary relation, which connects the surface composition with surface tension through order potential, surface coordination and volume ratio, is obtained. This has been applied to liquid Na–Cs alloys. Likewise bulk properties, surface segregation and surface tension of Na–Cs liquid alloys are also affected appreciably by the size difference and are anomalous around $C_{\text{Na}} = 0.8$.

KEY WORDS: Surface segregation, grand partition function.

1. INTRODUCTION

The phenomenon of surface segregation and surface tension in binary liquid alloys are important from the point of view of understanding many properties of physical significance such as catalytic activity of alloy catalyst, mechanical behaviour, kinetics of phase transformation etc. It is well known that the bulk properties are sensitive to size effect. Therefore we made an attempt to investigate the implications of size effect on the surface properties. A statistical mechanical approach^{1–3} based on the concept of layered structure near the interface has been found very useful for explaining surface properties of binary liquid alloys. The earlier approach of Prasad and Singh¹ has been improved upon to incorporate the effect of size difference on surface properties.

Na–Cs is a typical example of size effect (Cs-atom is 2.986 times bigger than Na-atom). Though the liquidus line is simply a deep eutectic but the free energy of mixing and concentration fluctuations^{4–6} ($q \rightarrow 0$) are quite asymmetric and exhibit anomalous variation around $C_{\text{Na}} = 0.8$. The X-ray and neutron diffraction experiments⁷ and electrical resistivity⁸ also indicate such behaviour around the same composition. In the context of such informations, the surface concentrations and surface tension of liquid Na–Cs alloys are studied as a function of bulk concentrations. The necessary formalism is given in sections-2, which follows, discussions and conclusion in sections 3 and 4 respectively.

2. FORMALISM

2.1 Construction of grand partition function at the surface and its solution

Let us consider a binary alloy $A-B$, which consists of N_A number of A atoms [= NC_A] and N_B number of B atoms [= NC_B] in the bulk phase; N being the total number of atoms, C_A and C_B are concentrations expressed in mole fractions such that $C_A + C_B = 1$. Following Prasad and Singh¹, the grand partition function at the surface, Ξ^s can be constructed as

$$\Xi^s = \sum_{E_s} q_{A_s}^{N_A^s}(T) q_{B_s}^{N_B^s}(T) \exp(\mu_A^s N_A^s + \mu_B^s N_B^s - E_s) / K_B T \quad (1)$$

where μ_i^s are chemical potentials of i (A or B atom) atom at the surface and E_s is the surface configurational energy. $q_{is}(T)$ is atomic partition function of i (A or B) atom at the surface and N_A^s, N_B^s, N^s, C_A^s and C_B^s refer to the quantities at the surface. It has been assumed that the species in the bulk and surface phases are in thermodynamic equilibrium. In the case of thermodynamic equilibrium,

$$\mu_A = \mu_A^s, \quad \mu_B = \mu_B^s \quad (2)$$

The terms without subscript and superscript 'S' represent the bulk. The basic problem, that is faced out in the solution of Eq. (1), lies in the definition of surface configurational energy, E_s . Prasad and Singh¹ in a very simple manner have expressed E_s as the product of order potential W [$W = Z \left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right)$; where $\varepsilon_{AA}, \varepsilon_{BB}$ and ε_{AB} are bond energies of $A-A, B-B$ and $A-B$ bonds respectively and Z is the coordination number] and effective number of $A-B$ contacts at the surface. It is given as

$$E_s = N^s W [p C_A^s C_B^s + q C_A C_B^s + C_B (C_A^s - C_A)] \quad (3)$$

where p and q are the fractions of total number of nearest neighbours made by an atom within its own layer and that in the adjoining layer, such that $p + 2q = 1$. As earlier¹, p and q have been treated as parameter and taken as $p = \frac{1}{2}$ and $q = \frac{1}{4}$.

Substituting E_s from Eq. (3) in Eq. (1), replacing the sum by its greatest term, differentiating the equation with respect to C_A and equating it to zero ($\partial \Xi^s / \partial C_A = 0$), we obtain a pair of equations for grand partition function at the surface Ξ^s , as

$$\Xi^s = \left[(q_{A_s}(T) / C_A^s) \exp \left(\frac{\mu_A - \{p(C_B^s)^2 + q(C_B)^2\} W}{K_B T} \right) \right]^{N^s} \quad (4a)$$

$$= \left[(q_{B_s}(T) / C_B^s) \exp \left(\frac{\mu_B - \{p(C_A^s)^2 + q(C_A)^2\} W}{K_B T} \right) \right]^{N^s} \quad (4b)$$

2.2 Standard thermodynamic relations

The grand partition function at the surface, Ξ^s , is related to surface tension of the alloy, σ , and surface area A , through the relation

$$\Xi^s = \exp\left(\frac{-\sigma A}{K_B T}\right) = \exp\left(\frac{-\sigma \cdot \alpha \cdot N^s}{K_B T}\right) \quad (5)$$

where $\alpha \left(= \frac{A}{N^s} \right)$ is the mean atomic surface area.

Further the chemical potential μ_i of i (A or B) atom is related to activity a_i through the relation

$$\mu_i = \mu_i^0 + K_B T \ln a_i \quad (6)$$

where μ_i^0 refers to pure component. Activity a_i and activity coefficient, γ_i , of i (A or B) component are connected through the relation

$$a_i = C_i \gamma_i \quad (7)$$

where C_i is the concentration of the components.

2.3 Expression for surface tension of the alloy

All the equations of section (2.2) [Eq. (5) to (7)] have been used in Eq. (4) to obtain a pair of equations for the surface tension of the alloy σ i.e.

$$\sigma = \sigma_A + \frac{K_B T}{\alpha} \ln \frac{C_A^s}{C_A} - \frac{K_B T}{\alpha} \ln \gamma_A + [p(C_B^s)^2 + q(C_B)^2] \frac{W}{\alpha} \quad (8a)$$

$$= \sigma_B + \frac{K_B T}{\alpha} \ln \frac{C_B^s}{C_B} - \frac{K_B T}{\alpha} \ln \gamma_B + [p(C_A^s)^2 + q(C_A)^2] \frac{W}{\alpha} \quad (8b)$$

where σ_A and σ_B are surface tension of pure components A and B respectively.

Further, we assume that γ_A^s and γ_B^s are activity coefficients of A and B components at the surface respectively and under very simplified picture, we express,

$$\ln \gamma_A^s = p(\ln \gamma_A \text{ containing surface concentration in place of bulk concentration}) + q \ln \gamma_A \quad (9a)$$

$$\ln \gamma_B^s = p(\ln \gamma_B \text{ containing surface concentration in place of bulk concentration}) + q \ln \gamma_B \quad (9b)$$

It is very simple to obtain expressions for activity coefficient at the surface (γ_A^s and γ_B^s) if one has proper expressions for bulk activity coefficient (γ_A and γ_B). In zeroth

approximation, where distribution of constituent atoms is completely random, γ_A and γ_B are given as

$$\ln \gamma_A = C_B^2 \frac{W}{K_B T} \quad (10a)$$

$$\ln \gamma_B = C_A^2 \frac{W}{K_B T} \quad (10b)$$

Using equations [Eq. (8) to Eq. (10)] one obtains a pair of equations for surface tension of the alloy σ , in terms of activity coefficient in the bulk and at the surface as

$$\sigma = \sigma_A + \frac{K_B T}{\alpha} \ln \frac{C_A^s}{C_A} + \frac{K_B T}{\alpha} \ln \frac{\gamma_A^s}{\gamma_A} \quad (11a)$$

$$= \sigma_B + \frac{K_B T}{\alpha} \ln \frac{C_B^s}{C_B} + \frac{K_B T}{\alpha} \ln \frac{\gamma_B^s}{\gamma_B} \quad (11b)$$

Size effect enters into Eq. (11) through γ_A and γ_B , for which we consider Flory's like expressions,

$$\ln \gamma_A = -\ln [C_A(1-r) + r] - \frac{C_B(1-r)}{C_A(1-r) + r} + \frac{C_B^2}{(1-bC_A)^2} \cdot \frac{W}{K_B T} \quad (12a)$$

$$\ln \gamma_B = \ln r - \ln [C_A(1-r) + r] - \frac{C_A(1-r)}{C_A(1-r) + r} + \frac{C_A^2(1-b)}{(1-bC_A)^2} \cdot \frac{W}{K_B T} \quad (12b)$$

where $b = (r-1)/r$; r being the ratio of volumes of B atom to A atom (Ω_B/Ω_A ; Ω_A and Ω_B are atomic volumes).

Using Eqs. (9), (11) and (12), one arrives at a pair of equations for surface tension for alloys of different sizes i.e.

$$\begin{aligned} \sigma = & \sigma_A + \frac{K_B T}{\alpha} \ln \frac{C_A^s}{C_A} + p \frac{K_B T}{\alpha} \left[\ln \frac{1-bC_A}{1-bC_A^s} - \frac{C_B \cdot b}{1-bC_A} \right. \\ & \left. + \frac{C_B \cdot b}{1-bC_A^s} + \frac{W}{K_B T} \left(\frac{(C_B^s)^2}{(1-bC_A^s)^2} - \frac{(C_B)^2}{(1-bC_A)^2} \right) \right] \\ & - q \frac{K_B T}{\alpha} \left[-\ln r(1-bC_A) + \frac{C_B b}{(1-bC_A)} + \frac{C_B^2}{(1-bC_A)^2} \cdot \frac{W}{K_B T} \right] \quad (13a) \end{aligned}$$

$$\begin{aligned} = & \sigma_B + \frac{K_B T}{\alpha} \ln \frac{C_B^s}{C_B} + p \frac{K_B T}{\alpha} \left[\ln \frac{1-bC_A}{1-bC_A^s} - \frac{b \cdot C_A^s}{1-bC_A^s} \right. \\ & \left. + \frac{b \cdot C_A}{1-bC_A} + (1-b) \frac{W}{K_B T} \left(\frac{(C_A^s)^2}{(1-bC_A^s)^2} - \frac{(C_A)^2}{(1-bC_A)^2} \right) \right] \\ & - q \frac{K_B T}{\alpha} \left[\ln r - \ln r(1-bC_A) - \frac{b \cdot C_A}{1-b \cdot C_A} + \frac{C_A^2(1-b)}{(1-bC_A)^2} \cdot \frac{W}{K_B T} \right] \quad (13b) \end{aligned}$$

Above equations can be solved numerically to determine the values of surface tension and surface composition.

3. RESULTS AND DISCUSSIONS

The pair of equations (13) has been used to compute surface tension and surface composition of Na–Cs liquid alloys. The basic inputs for obtaining the solution of above equation are order potential W , surface coordination fractions p and q , surface tension of pure components, atomic surface area and atomic volumes of the constituent elements.

The order potential W has been chosen as equal to $1.278 K_B T$ at $T = 383.15^\circ\text{K}$, so that the bulk properties including the concentration fluctuations are satisfactorily explained. The surface coordination fractions p and q are taken for closed packed structure ($p = \frac{1}{2}$ and $q = \frac{1}{4}$) and surface tension of pure components are taken from Smithel's reference book; $\sigma_{\text{Na}} = 0.1937 \text{ Nm}^{-1}$ and $\sigma_{\text{Cs}} = 0.0651 \text{ Nm}^{-1}$. The atomic surface area, α , has been computed by following relations⁹

$$\alpha = 1.102 N^{-2/3} \Omega^{2/3} \quad (14)$$

Experimentally obtained values⁴ of Ω have been used to compute α at each concentration. Using these quantities, Eq. (13) has been solved numerically to obtain surface tension, σ , and surface composition, C_i^s of Na–Cs liquid alloys as a function of bulk concentrations, C_i . The variations of surface tension and surface concentration with bulk concentrations have been presented in figures (1) and (2) respectively.

From Figure (1), it is clear that surface tension of Na–Cs liquid alloys at 383.15°K are always smaller than the ideal values $\sigma_{id} (= \sigma_{\text{Na}} C_{\text{Na}} + \sigma_{\text{Cs}} C_{\text{Cs}})$ for all bulk concentrations. The curvature is maximum around $C_{\text{Na}} = 0.8$.

The study of Figure (2) makes it clear that bigger atom (Cs) always segregate at the surface for all bulk concentrations of Cs. Even for small bulk concentrations of Cs, the surface seems to be quite enriched with the Cs atoms. For the alloy composition $\text{Na}_{0.9}\text{Cs}_{0.1}$ (bulk composition of alloy is 90% Na and 10% Cs) the surface composition of the alloy becomes $\text{Na}_{0.136}\text{Cs}_{0.864}$ (surface composition is 86.4% Cs and 13.6% Na). The surface composition (C_{Cs}^s) rises steeply with respect to bulk concentration.

Because of unavailability of experimental values, we could not compare out theoretical results.

4. CONCLUSION

An expression for surface tension and surface composition of binary liquid alloys, whose components differ appreciably in their sizes (Na–Cs system) has been developed. The computed values of surface composition indicate that bigger atoms (Cs) always segregate to the surface for all bulk compositions. Surface tension of Na–Cs alloys is always smaller than the ideal values, $\sigma_{id} (= C_{\text{Na}} \sigma_{\text{Na}} + C_{\text{Cs}} \sigma_{\text{Cs}})$. The study reveals that the surface composition is very sensitive to the size effect. Likewise the bulk properties,

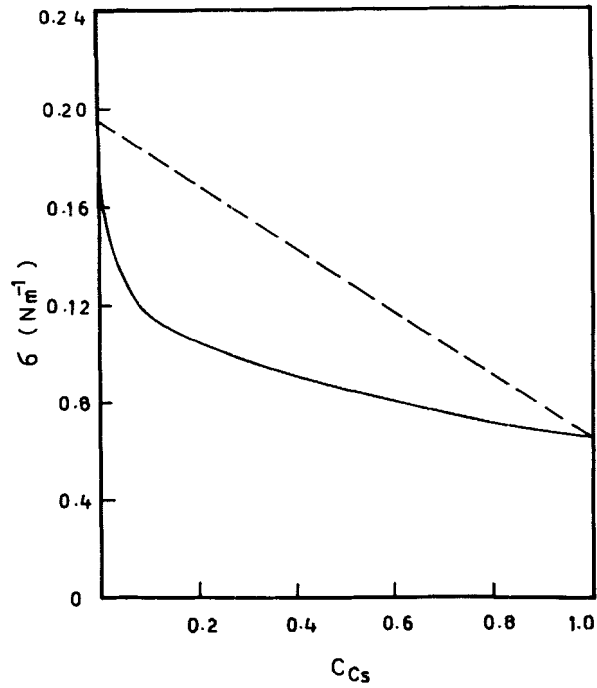


Figure 1 Surface tension, σ , of NaCs liquid alloy as a function of bulk concentration, C_{Cs} — and --- refer to present theory and ideal values respectively.

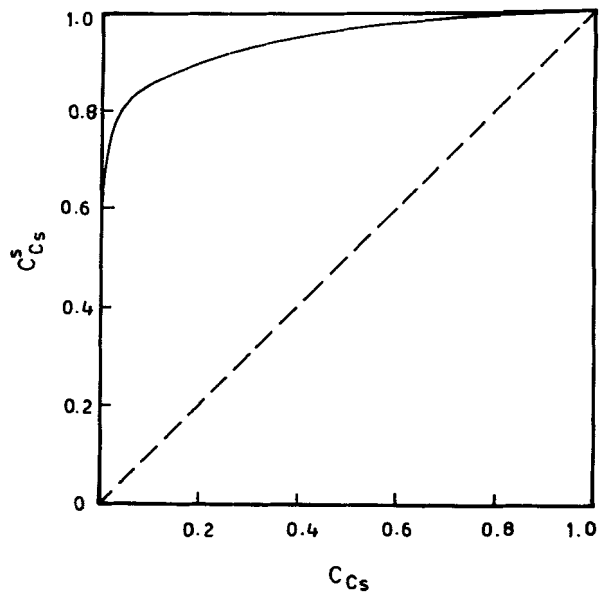


Figure 2 Surface concentration, C_{Cs}^s , of NaCs liquid alloys as a function of bulk concentration, C_{Cs} — refers to present theory.

maximum deviation in surface properties (surface tension and surface segregation) has been found to occur at $C_{\text{Na}} \simeq 0.8$.

References

1. L. C. Prasad and R. N. Singh, *Phys. Rev. B* **44**, 24, 13768 (1991).
2. K. S. Yeun, R. Speiser and D. R. Poirier, *Metall. Trans.* **20B**, 693 (1989).
3. D. R. Poirier and R. Speiser, *Metal. Trans.* **18A**, 1156 (1987).
4. F. E. Neale and N. E. Cusack, *J. Phys. F. Met. Phys.* **12**, 2839 (1982).
5. R. N. Singh and A. B. Bhatia, *J. Phys. F. Met. Phys.* **14**, 2309 (1984).
6. R. N. Singh and S. Sinha, *Phys. Of disordered Materials* (World Sc. Pub. Comp. Singapore, p. 1311)(1987).
7. M. J. Huijben, W. Vander Lugt, A. M. Reimert, J. Th. M. de Hosson and C Van Dijk; *Physica*, **97B**, 338 (1979).
8. B. P. Singh, V. N. Chaudhary and R. N. Singh, *Phys. Chem. Liq.* **23**, 211 (1991).
9. P. Laty, J. C. Joud and P. Desre, *Surf. Sc.* **60**, 109 (1976).