PHYSICAL REVIEW B VOLUME 44, NUMBER 24 15 DECEMBER 1991-II

# Surface segregation and concentration fluctuations at the liquid-vapor interface of molten Cu-Ni alloys

L. C. Prasad
*Department of Chemistry, T. N. B. College, Bhagalpur University, Bhagalpur 812007, India*

R. N. Singh
*Department of Physics, T. N. B. College, Bhagalpur University, Bhagalpur 812007, India*

(Received 13 March 1991)

The crossover of the surface segregation at the liquid-vapor interface of the liquid binary alloys has been examined for alloy order potential and the surface coordination number. The values of surface concentration and surface tension computed for liquid Cu-Ni alloys are in good agreement with the experimental observations. The surface effects are discussed in terms of concentration fluctuations in the long-wavelength limit.

Surface segregation, which manifests itself as a difference in composition between surface and bulk, is important to monitor many properties of liquid alloys including mechanical behavior, kinetics of phase transformation, and catalytic activity. Recent developments in experimental techniques (for example, see Sakurai *et al.*,[1] and references therein) and availability of data have aroused the interest of theoreticians to provide possible explanations. In particular, the experimental observation[1] of the crossover of surface segregation in the Cu-Ni system is interesting. Sakurai *et al.*[1] observed that Ni segregates to the surface in the terminal region $(0 < C \leq 0.16)$ of bulk Ni concentration. This is quite in contrast to earlier experimental and theoretical observations that Cu atoms always segregate to the surface for all bulk concentrations.

Among various theoretical models, the statistical approach,[2,3] which is based on the concept of the layered structure near the interface, is widely[4–7] used. The grand partition functions set up for the surface layer and that for the bulk provides a relation between surface $(C_i^s)$ and bulk $(C_i^b)$ concentrations. $C_i^s$ and $C_i^b$ are connected through surface tensions of the pure components, order energy, surface area, and the effective number of contacts at the surface. We intend to examine the crossover of surface segregation in the framework of the statistical mechanical model. We have also used the two partition functions to study the concentration fluctuations $[S_{CC}^s(0)]$ at the surface. Our investigation suggests that the concentration fluctuations at the surface are very much in contrast to the bulk fluctuations and could possibly be used to interpret the surface segregation.

Let a binary alloy consist of the $N_A$ number of $A$ atoms $[=NC_A^b]$ and $N_B$ number of $B$ atoms $[=NC_B^b]$, $N$ being equal to $N_A+N_B$; then the grand partition function for the bulk phase can be expressed[8] as

$$\Xi^b=\sum_E q_A^{N_A}(T)q_B^{N_B}(T)\exp[(\mu_A N_A+\mu_B N_B-E)/k_B T] \ , \tag{1}$$

where $\mu_i$ are chemical potentials of atoms $i$ ($A$ or $B$) and $q_i(T)$ are internal partition functions of individual atoms. $E$ is the configurational energy for the bulk phase and has been discussed elsewhere.[9] As in Eq. (1), it is possible to write an expression for the surface grand partition function

$$\Xi^s=\sum_{E_s} q_{A_s}^{N_A^s}(T)q_{B_s}^{N_B^s}(T)\exp[(\mu_A^s N_A^s+\mu_B^s N_B^s-E_s)/k_B T] \ , \tag{2}$$

where superscript and subscript $s$ refer to the quantities at the surface and $N^s=N_A^s+N_B^s[N_A^s=N^sC_A^s, N_B^s=N^sC_B^s]$. Further if the components in the surface and bulk phases are in thermodynamic equilibrium then

$$\mu_A=\mu_A^s, \quad \mu_B=\mu_B^s \ . \tag{3}$$

The basic problem in making Eq. (2) tractable is the definition of the surface configurational energy $E_s$. For simplicity we follow the regular solution approximation that $E_s$ can be expressed as the product of the order energy $W$ and the effective number of $A$-$B$ contacts at the surfaces. If we assume that $N_A^s$ and $N_B^s$ atoms mix randomly then

$$E_s=N^sW\{pC_A^sC_B^s+q[C_A^bC_B^s+C_B^b(C_B^s-C_A^b)]\}, \tag{4}$$

where $p$ and $q$ are the fractions of the total number of nearest neighbors made by an atom within its own layer and that in the adjoining layer such that $p+2q=1$. $W(=z[\varepsilon_{AB}-(\varepsilon_{AA}+\varepsilon_{BB})/2]$; $\varepsilon_{ij}$ are energies for $i-j$ pairs of atoms, $z$ is the coordination number) stands for order energy. For close-packed structure one has $p=\frac{1}{2}$ and $q=\frac{1}{4}$. But in view of the disordered structure and relaxation effect of the surface layer, it is suggested that $p$ and $q$ be treated as parameters. In developing Eq. (4) the invariance of the order energy has been explicitly assumed,

$$W=W^b=W^s \ . \tag{5}$$

Further $\Xi^s$ is also related to the surface tension ($\sigma$) and the surface area $A$ through the equilibrium thermodynamic relation

$$\Xi^s=\exp(-\sigma A/k_BT)=\exp(-N^s\sigma\alpha/k_BT)\ , \tag{6}$$

where $\alpha=A/N^s$ is the mean area of surface per atom. Equation (2) is now solved by substituting $E_s$ from Eq. (4), replacing the sum by the largest term and using the condition, i.e., $\partial\Xi^s/\partial C^s_A=0$. The equation thus obtained, in conjunction with Eq. (6), provides the requisite relations, i.e.,

$$\begin{aligned}\sigma=\sigma_A&+(k_BT/\alpha)\ln(C^s_A/C^b_A)\\&+[p(C^s_B)^2-(p+q)(C^b_B)^2]W/\alpha\ ,\end{aligned} \tag{7}$$

$$\begin{aligned}\sigma=\sigma_B&+(k_BT/\alpha)\ln(C^s_B/C^b_B)\\&+[p(C^s_A)^2-(p+q)(C^b_A)^2]W/\alpha\ .\end{aligned} \tag{8}$$

If one assumes that the atoms of the constituent species of the alloy mix ideally near the surface, i.e., $W=0$, then we obtain a simple analytic expression for surface concentration

$$C^s_\gamma=C^b_\gamma\exp[-\alpha(\sigma_A-\sigma_B)/k_BT]\ , \tag{9}$$

where $C^s_\gamma=C^s_A/C^s_B$ and $C^b_\gamma=C^b_A/C^b_B$. With the knowledge of surface tension or surface energy of the constituent species, Eq. (9) can readily be used to infer surface concentration.

The pair of Eqs. (7) and (8) can be solved numerically to obtain $C^s_i$ as a function of $C^b_i$. Obviously the surface concentration depends upon $\sigma_i$—the surface tension of the $i$th component in the pure state, $\alpha$—surface area per atom, order energy $W$, and the coordination fractions. This approach is useful because it can be used to investigate the dependence of surface composition on order energy and the surface coordination. We intend to investigate it with special reference to liquid Cu-Ni alloys where

$$\sigma_A(A\equiv\mathrm{Cu})=1.262\ \mathrm{Nm}^{-1},\ \sigma_B(B\equiv\mathrm{Ni})=1.741\ \mathrm{Nm}^{-1}\ . \tag{10}$$

The surface area $\alpha$ was calculated following the relation[10]

$$\alpha_i=1.102N^{-2/3}\Omega_i^{2/3}\ . \tag{11}$$

$N$ is the Avogadro's number and $\Omega_i$ is the atomic volume. Mean surface area $\alpha$ of the alloy was calculated from the relation $\alpha=\sum_i C_i\alpha_i$.

In order to determine $W$ for Cu-Ni, we use a simple relation[8]

$$G^{xs}_M/Nk_BT=\ln 2^{z/2}[1+\exp(-W/zk_BT)]^{-z/2}\ . \tag{12}$$

$G^{xs}_M$ is the excess free enregy of mixing and $z$ is the coordination number. The observed value[11] of $G^{xs}_M$ yields $W/k_BT=0.817$. Equations (7) and (8) have been solved numerically to obtain $C^s_i$ for a close-packed structure. The results of Cu-Ni (see Fig. 1) are compared with experiments.[1,12,13] The theoretical values for $W=0.817/k_BT$ and the experimental observation of Auger spectroscopy[12,13] indicate that Cu atoms always segregate at the surface. Though the present theory exhibits some deepening near the terminal region ($C^b_{\mathrm{Ni}}\leq 0.2$), the crossover as observed in the experiment of time-of-flight atom probe[1] is not achieved.

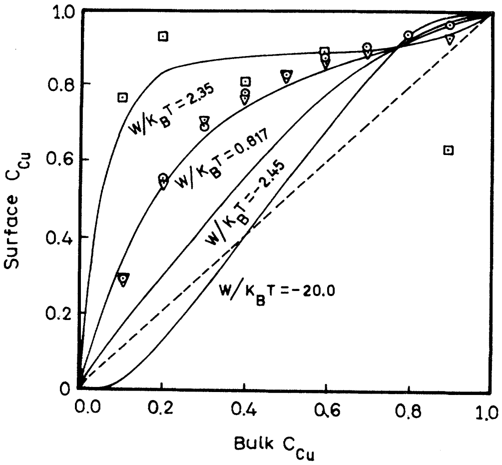

FIG. 1. $C^s_{\mathrm{Cu}}$ as a function of $C^b_{\mathrm{Cu}}$. ——, theory with different order energy; experimental points: △△△ , Takasu and Shimizu (Ref. 13); ⊙⊙⊙, Watanabe, Hashiba, and Yamashina (Ref. 12); ⊡⊡⊡, Sukurai *et al.* (Ref. 1).

For a given system, i.e., $\sigma_i$ and $\alpha$ are fixed, Eqs. (7) and (8) can further be simplified for a close-packed structure, i.e,

$$\begin{aligned}\ln(C^s_A/C^s_B)&+p(W/k_BT)[C^s_B-C^s_A]\\&=1.1422+\ln(C^b_A/C^b_B)\\&\quad+[(p+q)W/k_BT](C^b_B-C^b_A)\ .\end{aligned} \tag{13}$$

It is of interest to use Eq. (13) to examine the crossover, in general, of surface segregation as a function of $W$. The results (Fig. 1) indicate that the surface segregation depends considerably on the order energy. With the increasing positive value of the order energy, the Cu atoms at the surface start depleting fast in the terminal region ($C^b_{\mathrm{Cu}}>0.8$) of Cu bulk rich end. As soon as one approaches $W\approx 5.5k_BT$, the crossover occurs indicating that Ni atoms segregate at the surface at the Cu bulk rich end. But obviously such a $W=5.5k_BT$ is quite large in comparison to what one derives ($W=0.817k_BT$) from Eq. (12) for the bulk phase. It is likely that $W$ at the surface is different than the bulk phase, but such a large deviation seems difficult, at present, to be accommodated for the Cu-Ni system. Contrary to a large positive $W$, Eq. (13) also suggests a crossover for large negative ordering energy (say $W/k_BT\leq -5.71$). But unlike earlier, Ni atoms segregate here at the surface in the terminal region where the bulk phase is quite rich in Ni atoms. Thus it is possible to obtain both kinds of crossover for large positive and negative order energy.

The value of $C^s_i$, as shown in Fig. 1, has also been used to compute surface tension from Eq. (7). The results (Fig. 2) suggest that $\sigma$ is very sensitive to the choice of $W$. The theoretical values of Cu-Ni are in good agreement with the experimental observations.[14]

The effect of the surface coordination on surface composition has been studied by changing the value of $p$, say $p=0.25$, 0.5, 0.75, 0.90. The corresponding $q$ has been obtained from the condition $p+2q=1$. The values of $p$, respectively, correspond to surface coordination, $z^s=7.5$, 9, 10.5, and 11.4 for close-packed bulk structure. The values of $C_i^s$ computed for different values of $p$ and fixed $W(=0.817k_BT)$ are plotted in Fig. 3. It suggests that the surface concentration is not sensitive to the surface coordination the same way as to the order energy.

Further, the surface grand partition function as in Eq. (2) can be solved following the works by Singh *et al.*[8,15] for the bulk phase to obtain the long-wavelength limit ($q \rightarrow 0$) expression for the concentration fluctuations[16] at the surface, i.e.,

$$S^s_{CC}(0)=C^s_A C^s_B[1+(z^s/2\beta^s)(1-\beta^s)]^{-1}\,, \tag{14}$$

with

$$\beta^s=\{1+4C^s_A C^s_B[\exp(2W/z^s k_B T)-1]\}^{1/2}\,, \tag{15}$$

where $z^s$ is the coordination number of the surface atom and in the present scheme it is given by $(p+q)z$. If at a surface, the constituent atoms mix ideally, i.e., $W=0$, one has

$$S^s_{CC}(0,\text{ideal})=C^s_A C^s_B\,. \tag{16}$$

Obviously $S^b_{CC}(0)$ for bulk phase can be readily obtained by setting $C_i^s \rightarrow C_i^b$ and $z^s \rightarrow z$. We observe that even for ideal mixing the concentration fluctuations at the surface $[S^s_{CC}(0,\text{ideal})]$ are quite in contrast to bulk $[S^b_{CC}(0,\text{ideal})=C^b_A C^b_B]$ values (Fig. 4) due to difference in $C_i^b$ and $C_i^s$.

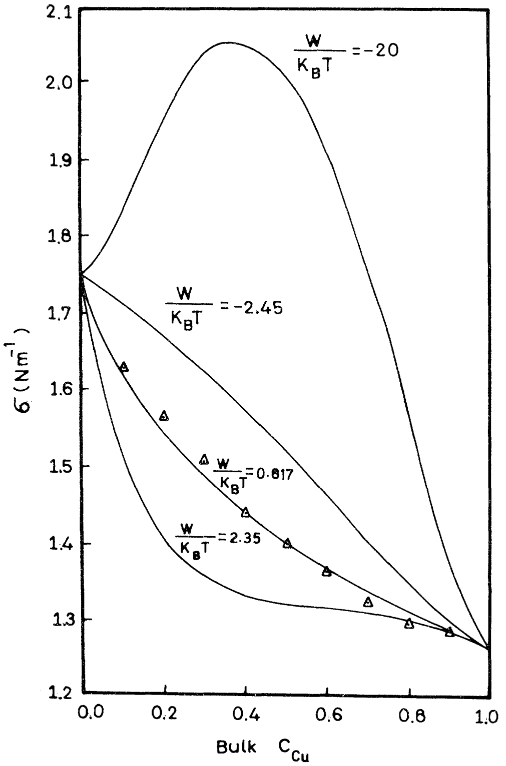

FIG. 2. Surface tension ($\sigma$ in Nm$^{-1}$) of liquid binary alloys for different order energy. $W/k_BT=0.817$ corresponds to the Cu-Ni system. △△△ refer to experimental values (Ref. 14).

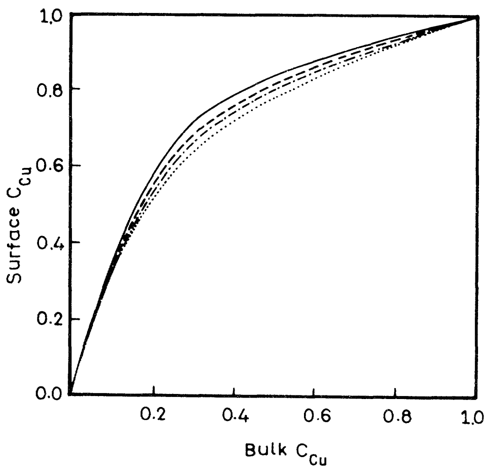

FIG. 3. The effect of surface coordination on the surface concentration of liquid Cu-Ni alloys: · · · ·, —·—·—·, — — —, and —— correspond to $p=0.25$, 0.50, 0.75, and 0.90, respectively.

It is of interest to discuss $S_{CC}(0)$ because it is directly

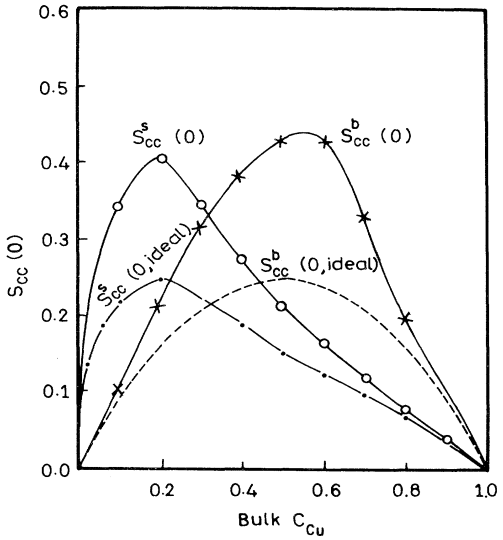

FIG. 4. Long-wavelength limit of the concentration fluctuations of liquid Cu-Ni alloys. —×—×—×—×—, $S^b_{CC}(0)$ directly computed from activity data; — — —, $S^b_{CC}$ (0, ideal); o–o–o–o, $S^s_{CC}(0)$ computed from theoretical expression (14); and —·—·—·, $S^s_{CC}$ (0, ideal).

linked[9] to the order and the segregation in binary liquid alloys. $S_{CC}^{b}(0)$ for liquid Cu-Ni alloys can also be obtained directly from the measured activity data

$$S_{CC}^{b}(0)=C_{\mathrm{Ni}}^{b}a_{\mathrm{Cu}}\left[\frac{\partial a_{\mathrm{Cu}}}{\partial C_{\mathrm{Cu}}}\right]^{-1}=C_{\mathrm{Cu}}^{b}a_{\mathrm{Ni}}\left[\frac{\partial a_{\mathrm{Ni}}}{\partial C_{\mathrm{Ni}}}\right]^{-1}, \quad (17)$$

where $a_{\mathrm{Cu}}$ and $a_{\mathrm{Ni}}$ are the activities of Cu and Ni, respectively, in the bulk phase.

$S_{CC}^{b}(0)$ computed from Eq. (17) is plotted in Fig. 4 which indicates that segregation in bulk occurs at all concentrations being maximum around $C_{\mathrm{Cu}}^{b}=0.6$. $S_{CC}^{b}(0)$ is also asymmetrical around the equiatomic composition. The study suggests that there is a tendency of weakening of bulk segregation towards the terminal region of the Cu rich end.

Finally Eq. (14) has been used to compute the concentration fluctuations $S_{CC}^{s}(0)$ at the surface. This has been done by taking $W/k_BT=0.817$ and $C_i^s$ as determined earlier for the Cu-Ni system. The value of $S_{CC}^{s}(0)$ is quite in contrast to $S_{CC}^{b}(0)$. The surface concentration fluctuations rise quickly to maximum and fall through a concave surface to minimum. The width of the maxima of $S_{CC}^{s}(0)$ is small in comparison to $S_{CC}^{b}(0)$. Though $S_{CC}^{s}(0)$ suggests that segregation occurs at the surface, the identification of segregating atoms from $S_{CC}^{s}(0)$ needs to be investigated.

---

[1] T. Sakuari, T. Hashizume, A. Jimbo, and A. Sakai, Phys. Rev. Lett. **55**, 514 (1985).

[2] E. A. Guggenheim, *Mixtures* (Oxford University Press, Oxford, England, 1952).

[3] T. P. Hoar and D. A. Melford, Trans. Faraday Soc. **53**, 315 (1957).

[4] K. S. Yeum, R. Speiser, and D. R. Poirier, Metall. Trans. **20B**, 693 (1989).

[5] D. R. Poirier and R. Speiser, Metall. Trans. **18A**, 1156 (1987).

[6] Yi-Chen Cheng, Phys. Rev. B **28**, 2937 (1983).

[7] J. L. Moran-Lopez and L. M. Falicov, Phys. Rev. B **18**, 2549 (1978).

[8] R. N. Singh, I. K. Mishra, and V. N. Singh, J. Phys. Condens. Matter **2**, 8457 (1990).

[9] R. N. Singh, Can. J. Phys. **65**, 309 (1976).

[10] P. Laty, J. C. Joud, and P. Desre, Surf. Sci. **60**, 109 (1976).

[11] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (American Society for Metals, Metal Park, OH, 1973).

[12] K. Watanabe, M. Hashiba, and T. Yamashina, Surf. Sci. **61**, 483 (1976).

[13] Y. Takasu and H. Shimizu, J. Catal. **29**, 479 (1973).

[14] V. V. Fesenko, V. N. Eremenko, and M. I. Vasilu, Zh. Fiz. Khim. **35**, 1750 (1961).

[15] R. N. Singh and I. K. Mishra, Phys. Chem. Liq. **18**, 303 (1988).

[16] A. B. Bhatia and D. E. Thornton, Phys. Rev. B **2**, 3004 (1970).