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Surface segregation in the hydrogen-adsorbed Cu-Ni alloy

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Electronic theory has been used to study the effect of chemisorption of a monolayer of H adatoms on the segregation behavior in the Cu-Ni alloy. The theory gives results in qualitative agreement with the experimental results of Sinfelt *et al.* It has been found that the chemisorption of H adatoms reduces the Cu segregation to the surface when contrasted with the Cu segregation in the clean Cu-Ni alloy. The segregation in the present calculation is also less compared to the chemisorption-induced surface segregation obtained from the pair bond model.

I. INTRODUCTION

There is enough experimental as well as theoretical evidence[1-5] to suggest that in a clean Cu_xNi_{1-x} alloy system copper atoms segregate to the surface. There have been, however, relatively few studies[6,7] on how the segregation behavior in this alloy is affected by the presence of chemisorbed species. This is due to the fact that in both experiment and theory the introduction of adsorbates brings additional complications. For example, in the experimental method of work-function (W) measurement one has to identify the two contributions to the change in W, one due to the change in surface composition and the other due to the presence of adsorbates. In the method of low-energy ion scattering (LEIS),[8] similarly, one has to distinguish between the contributions to the scattered yield due to the changing surface composition and the adsorbates. In the theory, on the other hand, one has to develop a microscopic electronic theory of chemisorption-induced surface segregation, which requires involved calculations. An alternative model, called the "pair bond model," was therefore developed to obtain a first physical understanding of chemisorption-induced surface segregation.[7] It is the main purpose of the present work to extend, for the first time, the existing tight-binding electronic theory to calculate the surface segregation in the Cu-Ni alloy system in the presence of a static monolayer of hydrogen adatoms. In physical terms, the chemisorbed monolayer is assumed to remain static while the surface composition undergoes thermodynamic changes. The results have also been compared with the experimental as well as other theoretical results on this system.[6,7] Secondly, it is also argued in this work that the experimental results of Sinfelt, Carter, and Yates[6] give the chemisorption-induced surface segregation rather than the segregation in clean Cu-Ni alloys by the H_2 adsorption technique, as is often quoted in the literature.[5,8] In Sec. II we discuss the theoretical model used in this work and in Sec. III we present our results and discussions.

II. THEORETICAL MODEL

We extend the theoretical model of Mukherjee, Morán-Lopez, Kumar, and Bennemann[5] to our chemisorption system H/Cu_xNi_{1-x}. To simplify the calculations we assume that a monolayer of H adatoms is chemisorbed on the top positions of the (111) surface of a Cu-Ni alloy. We distinguish thereby the two layers, namely, the chemisorbed monolayer and the surface layer of the substrate from the rest of the substrate layers which we consider as bulk. The bulk concentration x_b, say, is externally controlled, while the monolayer is assumed to be static. Under these conditions, the free energy of the system may be expressed as a function of the bulk alloy concentration x_b and the surface concentration x_s. For a particular temperature T and bulk concentration x_b the free energy has to be minimized with respect to x_s subject to the constraint that the total numbers of atoms and electrons in the system are fixed. We obtain thereby a value of x_s for a particular value of x_b.

Mathematically, we have to minimize an effective free energy F' given by[5]

$$F' = \sum_{\lambda=0}^{\infty} E_\lambda(\Theta=1, x_1=x_s, x_2=x_3=\cdots=x_b) - TS - \mu\sum_{\lambda=0}^{\infty} x_\lambda - \nu\sum_{\lambda=0}^{\infty}\langle n_\lambda\rangle \,, \tag{1}$$

where λ is the layer index, $\lambda=0$ indicating the chemisorbed monolayer, $\lambda=1$ the substrate surface layer, and so on. $\theta=1$ indicates a monolayer of H adatoms. E_λ denotes the internal energy of an atom in the λth layer; T and S are the temperature and entropy of the system, respectively; μ and ν are the Lagrange multiplers arising from the two constraints conserving the total number of atoms and electrons in the system. $\langle n_\lambda\rangle$ denotes the average number of electrons on an atom in the λth plane.

To calculate E_λ from the densities of states $\rho_\lambda(E)$ we use the tight-binding Hamiltonian

$$H = \sum_i \varepsilon_i |i\rangle\langle i| + \sum_{\substack{i,j \\ (i\neq j)}} V_{ij} |i\rangle\langle j| \,, \tag{2}$$

where i is the site index for the total chemisorption system; ε_i and V_{ij} are the site energy and the hopping interaction energy between the ith and jth site, respectively. For simplicity of calculations, again, we consider only the d orbitals; and to avoid self-consistency we assume that the site energies are modified to take into account all kinds of correlation energies including the intra-atomic electron-

electron Coulomb interactions. For example, for the H/Ni system we consider the adsorbate level as $\varepsilon_a \approx -10.6$ eV, about 3 eV above the adsorbate level in the free state. The calculation of $\rho_\lambda(E)$ is then straightforward. We use the mixed Bethe-lattice model[5] to calculate $\rho_\lambda(E)$. $E_\lambda(E)$ may then be calculated from the relation

$$E_\lambda = \int_{-\infty}^{E_F} E\rho_\lambda(E)dE \ . \tag{3}$$

For S we consider the expression

$$S = -k_B \sum_\lambda [x_\lambda \ln x_\lambda + (1-x_\lambda)\ln(1-x_\lambda)] \ . \tag{4}$$

Calculation of x_s is then done by minimizing F' numerically.

III. RESULTS AND DISCUSSIONS

The metal parameters used in the calculations are the bandwidths of the constituents of the alloy, the mean energies of the d band, and the number of d electrons. The d-band widths of Cu and Ni are taken to be 3.34 and 4.3 eV, respectively.[5] The difference between the mean energies $\varepsilon_{\mathrm{Ni}} - \varepsilon_{\mathrm{Cu}} = 1.8$ eV; and the band fillings are taken equal to 10 and 9.4 electrons per atom for the Cu and the Ni atom, respectively. The Fermi energy of the system has been calculated using the formula

$$\int_{-\infty}^{E_F} \rho_{\mathrm{av}}(E)dE = x_b N_{\mathrm{Cu}} + (1-x_b)N_{\mathrm{Ni}} \ , \tag{5}$$

where $\rho_{\mathrm{av}}(E)$ is the average density of states and $N_{\mathrm{Cu}}=10$ and $N_{\mathrm{Ni}}=9.4$ electrons/atom. The Cu-Cu, Ni-Ni, and Cu-Ni hopping parameters are assumed to be the same for surface-surface, surface-bulk, and bulk-bulk hopping. The adsorbate-substrate hopping parameters are chosen to be $V_{\mathrm{Ni\text{-}H}} = 1.05$ eV and $V_{\mathrm{Cu\text{-}H}} = 1.0$ eV. The adsorbate-adsorbate parameter $V_{\mathrm{H\text{-}H}}$ is taken to be 0.05 eV. These values are chosen to ensure that the Ni—H bonding is stronger than the Cu—H bonding and that they yield a magnitude for the chemisorption energy compatible with the experimental chemisorption energy for a fully hydrogen-covered ($\theta=1$) Ni or Cu surface. We have noted that increasing the $V_{\mathrm{H\text{-}H}}$ parameter to 0.1 does not drastically affect the segregation behavior in the alloy. Under these conditions the calculated results are shown in Figs. 1-4.

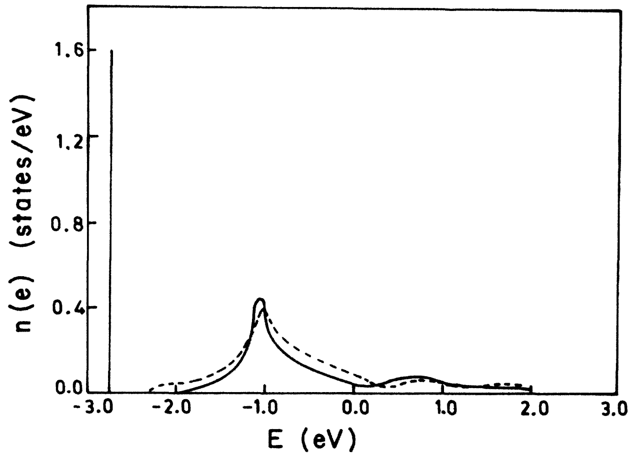

FIG. 1. Density of states curves at an adsorbate site: solid line, $x_b = 0.25$ and dashed line, $x_b = 0.5$.

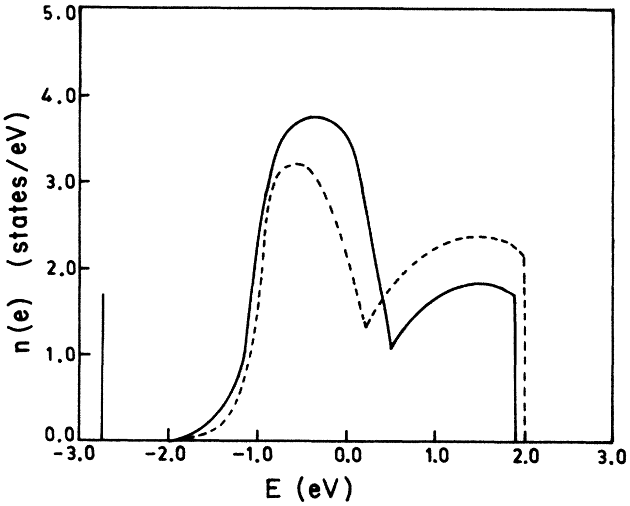

FIG. 2. Average density of states curves at a surface site: solid line, $x_b = 0.5$ and dashed line, $x_b = 0.25$.

Figures 1-3 show some typical local-density-of-states curves as obtained from our present model calculation. The curves are self-explanatory. The vertical lines shown below the lower band edge are the split-off states due to the adsorbate-substrate interaction. In Fig. 4 we present the segregation results calculated from the present model (curves a and b) along with the experimental results of Sinfelt *et al.*[6] (curve e) and the theoretical results of Tománek, Mukherjee, Kumar, and Bennemann[7] based on the pair bond model (curves c and d). Three features are to be noted. First, the chemisorption of a monolayer of hydrogen atoms lowers the Cu segregation with respect to the clean-surface Cu segregation. Second, in the high-

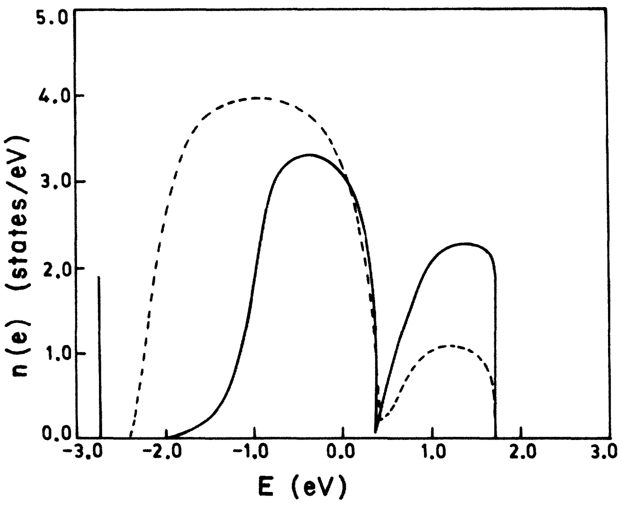

FIG. 3. Average density of states curves at a surface site: $x_b = 0.75$: solid line, in presence of adsorbates; dashed line, in clean alloy.

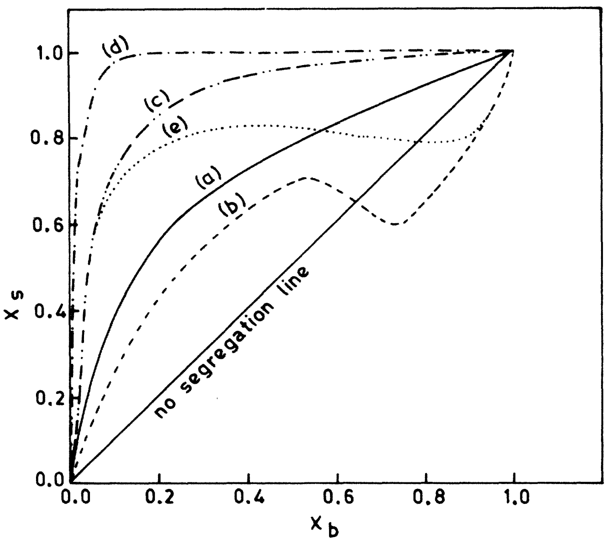

FIG. 4. Segregation behavior in the H/Cu_xNi_{1-x} chemisorption system. (a) and (b), present results; (c) and (d), pair bond model results (Ref. 7); and (e), the experimetal results of Sinfelt *et al.* (Ref. 6). (a) and (d) are results in the absence of chemisorption, and (b) and (c) are results in the presence of H adatoms.

Cu-concentration regime Ni seems to segregate as is found in the experiment of Sinfelt *et al.* Please note the crossover in our theoretical curve as well as in the experimental curve. Third, the present theoretical segregation curves indicate less Cu segregation compared to those obtained from the pair bond model of Tománek *et al.*[7] Physically, the decrease in Cu segregation in the presence of H adatoms may be understood from the following simple arguments: In the clean Cu-Ni alloy Cu atoms segregate to the surface. We may visualize this phenomenon as one in which a segregation energy, Q_{seg} (say), is required to exchange a surface Cu atom with a bulk Ni atom. The Ni-H chemisorption bond being stronger than the Cu-H chemisorption bond, in the presence of hydrogen adatoms the Ni atoms would feel a stronger pull towards the surface than the pull felt by the Cu atoms. As a result, the net energy required to exchange a surface Cu atom with a bulk Ni atom (Q'_{seg}, say) will be less compared to Q_{seg} of clean Cu-Ni alloys. Thus, in the presence of hydrogen adatoms there would be a reduction in Cu segretation to the surface compared to the segregation in clean Cu-Ni alloys.

It is interesting to note here that the experimental results of Sinfelt *et al.*, which were obtained by hydrogen adsorption method, are often wrongly quoted in the literature to give the surface composition of a clean Cu-Ni alloy. Furthermore, they are also wrongly compared with the other theoretical and experimental results on the segregation behavior in the clean Cu-Ni alloy system.[5,8] As a result, all these results vary drastically from the results of Sinfelt *et al.* (See, for example, Fig. 18.6 in Ref. 8.) We would like to comment here that in order to interpret the results of Sinfelt *et al.* one has to consider segregation in the presence of the chemisorbed hydrogen monolayer as done in the present work.

Summarizing, a simplified electronic theory based on the tight-binding Anderson Hamiltonian in the mixed Bethe-lattice scheme, has been used to study the phenomenon of chemisorption-induced surface segretation in a hydrogen-covered Ni-Cu alloy system—a phenomenon known since the early 1970's for other transition-metal–noble-metal alloys.[9,10] In view of the fact that this is a model calculation with assumptions made on (i) the geometrical configuration of the chemisorbed overlayer, (ii) the electronic bands playing a role in the process, (iii) the electron-electron correlation, and (iv) the various hopping parameters, etc., the qualitative correct trend obtained by the present model calculation may be considered to be satisfactory. Further studies with self-consistency and more realistic parametrization may lead to still better understanding of the phenomenon for the Cu-Ni system.

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