The mutual influence of chemisorption and surface segregation: calculation of the chemisorption energy of O or CO on Ni-Cu alloy

## LETTER TO THE EDITOR

# The mutual influence of chemisorption and surface segregation: calculation of the chemisorption energy of O or CO on Ni–Cu alloy

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**Abstract.** The Green's function method and the chemisorption theory of Einstein and Schrieffer are used to calculate the chemisorption energy of O or CO on a Ni–Cu disordered binary alloy surface using the average $T$-matrix approximation. The change of surface segregation due to chemisorption is investigated in detail. From the chemisorption point of view, the behaviour of O resembles that of CO to a certain extent. The calculated results show that the chemisorption of O/Ni–Cu and CO/Ni–Cu systems can all constrain surface segregation, resulting in more stable chemisorption.

In our previous paper [1], we studied the chemisorption of the CO/Ni–Cu system using the coherent-potential approximation (CPA) and obtained some important conclusions: that the chemisorption of the system can change surface concentration, constrain surface segregation and make the chemisorption energy decrease. In this letter, we employ the average $T$-matrix approximation (ATA) and the Green's function (GF) method to study further the chemisorption properties of O/Ni–Cu and CO/Ni–Cu systems. The purpose of the present work is to emphasize the mutual influence of chemisorption and surface segregation. Within the one-dimensional tight-binding approximation, the chemisorption system consists of the effective adsorbate [1] interacting with a semi-infinite, monatomic chain of Ni–Cu disordered binary alloy (DBA). The model of a substitutional DBA developed by Ueba *et al* [2] is adopted. The virtual-crystal Hamiltonian for the substrate is then

$$H_{\mathrm{v}} = \sum_{i=1}^{\infty} \{\alpha_i |i\rangle\langle i| - T(|i\rangle\langle i+1| + |i+1\rangle\langle i|)\}. \tag{1}$$

In (1), the effective bond strength $-T$ between nearest-neighbour atoms is concerned with the bulk concentration $X_{\mathrm{b}}$ of the A component. On confining surface segregation to the first (surface) layer, the virtual-crystal electronic energy [1] at atom $i$ is

$$\alpha_i = \begin{cases} X_{\mathrm{b}}\Delta + \epsilon_{\mathrm{B}} & i > 1 \\ X_s\Delta + \epsilon_{\mathrm{B}} & i = 1, \text{ before chemisorption} \\ X_c\Delta + \epsilon_{\mathrm{B}} & i = 1, \text{ after chemisorption} \end{cases} \tag{2}$$

where $\Delta = \epsilon_{\mathrm{A}} - \epsilon_{\mathrm{B}}$, $\epsilon_{\mathrm{A}}$ ($\epsilon_{\mathrm{B}}$) is the electronic energy of an A (B) atom and $X_s$ ($X_c$) is the surface concentration of the A component at the site 1 of the DBA before (after) chemisorption.

Within the ATA, the self-energy [2,3] associated with the $i$th atomic site is introduced as

$$\xi_i = \begin{cases} \xi_b & i > 1 \\ \xi_s & i = 1, \text{ before chemisorption} \\ \xi_c & i = 1, \text{ after chemisorption.} \end{cases} \tag{3}$$

In (3),

$$\xi_i = \frac{\Delta^2 X_b \, (1 - X_b) F_i(Z_1)}{1 - \Delta(1 - 2X_b) F_i(Z_1)} \qquad i = b, s, c \tag{4}$$

where $F_b(Z_1)$ is a diagonal element of the GF for the infinite DBA under the virtual-crystal approximation, and $F_s(Z_1)$ ($F_c(Z_1)$) is that of the surface GF at site 1 before (after) chemisorption. They can be determined by the following:

$$F_b(Z_1) = 1 / \left( 2T\sqrt{Z_1^2 - 1} \right) \tag{5}$$

$$F_s(Z_1) = \left[ F_{s0}^{-1}(Z_1) - (X_s - X_b)\Delta \right]^{-1} \tag{6}$$

$$F_c(Z_1) = \left[ F_s^{-1}(Z_1) - \gamma^2 G_a \right]^{-1} \tag{7}$$

where

$$Z_1 = (E + i0^+ - \alpha_b)/2T \tag{8}$$

$$F_{s0}(Z_1) = \left( Z_1 - \sqrt{Z_1^2 - 1} \right)/T. \tag{9}$$

The effective GF of the effective adsorbate is defined by

$$G_a = (E - E_{\text{eff}} + i0^+)^{-1} \tag{10}$$

where $E_{\text{eff}}$ is the effective level of the effective adsorbate attached to the surface atom of the substrate by a bond of energy $\gamma$ which can be represented by

$$\gamma = X_c\gamma_A + (1 - X_c)\gamma_B. \tag{11}$$

Before chemisorption the effective Hamiltonian for the semi-DBA is

$$H_{\text{eff}} = H_v + \sum_{i=1}^{\infty} \xi_i |i\rangle\langle i| \tag{12}$$

and, therefore, the effective surface GF is

$$G_s = \left[ F_{s0}^{-1}(Z_2) - (\xi_a - \xi_b) - (X_s - X_b)\Delta \right]^{-1} \tag{13}$$

where

$$Z_2 = \left( E + i0^+ - \alpha_b - \xi_b \right)/2T. \tag{14}$$

After chemisorption the effective Hamiltonian of the chemisorption system is

$$H_{\text{eff}}^c = E_{\text{eff}}|a\rangle\langle a| + H_{\text{eff}} + \left[ (X_c - X_s)\Delta + (\xi_c - \xi_s) \right]|1\rangle\langle 1| + \gamma(|a\rangle\langle 1| + |1\rangle\langle a|). \tag{15}$$

According to the chemisorption theory of Einstein and Schrieffer [4], the change in the density of states caused by chemisorption is

$$\Delta\rho(E) = -(1/\pi)\text{Im} \, (\partial/\partial E)\left[ \ln \det (1 - G^0 V) \right] \tag{16}$$

where

$$G^0 = \begin{bmatrix} G_a & 0 \\ 0 & G_s \end{bmatrix} \tag{17}$$

$$V = \begin{bmatrix} 0 & \gamma \\ \gamma & (X_c - X_s)\Delta + (\xi_c - \xi_s) \end{bmatrix}. \tag{18}$$

The chemisorption energy can be written as

$$\Delta E = 2 \int_{-\infty}^{E_F} (E - E_F)\, \Delta\rho(E)\, \mathrm{d}E \qquad (19)$$

where $E_F$ is the Fermi level. A direct calculation of this integral is rather cumbersome (the integrand can have sharp peaks due to the presence of resonance). The technique of complex-energy-plane integration [5] is, therefore, adopted to calculate the chemisorption energy, i.e.,

$$\Delta E = \frac{2}{\pi} \int_0^{\infty} \mathrm{Re}\, f(Z)\, \mathrm{d}y \qquad (20)$$

where

$$f(Z) = (Z - E_F)(\partial/\partial Z) \ln\{1 - [(X_c - X_s)\Delta + (\xi_c - \xi_s)]\,G_s(Z) - \gamma^2 G_a(Z)G_s(Z)\}. \qquad (21)$$

In (20) and (21),

$$Z = E_F + iy \qquad (22)$$

where the $y$ are real numbers.

Table 1. Parameters for pure metals; Ni, Cu; all energies are in eV.

| Element | $\epsilon_{a(B)}$ | $E_F$ | $\gamma_{A(B)}/O$ | $\gamma_{A(B)}/CO$ |
|---------|-------|-------|-------|-------|
| | | | Parameter | |
| Ni | −6.260 | −4.500 | 4.217 | 2.763 |
| Cu | −7.370 | −4.460 | 4.725 | 3.320 |

Table 2. Surface concentrations $X_s$, $X_c/O$ and $X_c/CO$ versus bulk Ni concentration $X_b$ for segregated Ni–Cu alloy.

| $X_b$ | $X_s$ | $X_c/O$ | $X_c/CO$ |
|-------|-------|---------|----------|
| 0.0 | 0.00000 | 0.00000 | 0.00000 |
| 0.1 | 0.00009 | 0.18314 | 0.04314 |
| 0.2 | 0.00020 | 0.33530 | 0.09209 |
| 0.3 | 0.00035 | 0.46374 | 0.14813 |
| 0.4 | 0.00054 | 0.57359 | 0.21290 |
| 0.5 | 0.00081 | 0.66863 | 0.28863 |
| 0.6 | 0.00122 | 0.75165 | 0.37834 |
| 0.7 | 0.00189 | 0.82481 | 0.48632 |
| 0.8 | 0.00324 | 0.88975 | 0.61875 |
| 0.9 | 0.00725 | 0.94781 | 0.78502 |
| 1.0 | 1.00000 | 1.00000 | 1.00000 |

Utilizing the pure-substrate parameters found in table 1, calculations of the chemisorption energies of the O/Ni–Cu and CO/Ni–Cu systems have been performed over the full range of bulk concentrations ($X_b$). The values of the effective energy $E_{eff}$ of O (CO) and the adsorbate coverage $\theta$ are chosen to be −7.5 eV (−7.7 eV) and 0.5, respectively. The surface component concentration $X_s$ ($X_c$) is calculated, employing the expression for the surface concentration of an alloy $A_x B_{1-x}$ before
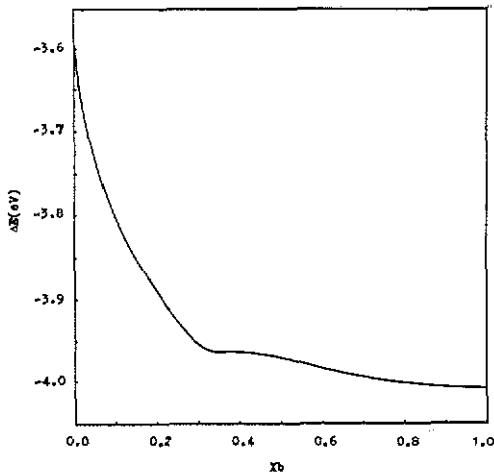
**Figure 1.** Chemisorption energy $\Delta E$ for O/Ni–Cu versus bulk Ni concentration $X_b$, taking into consideration the change of surface segregation due to chemisorption.

**Figure 2.** Chemisorption energy $\Delta E$ for CO/Ni–Cu versus bulk Ni concentration $X_b$, taking into consideration the change of surface segregation due to chemisorption.
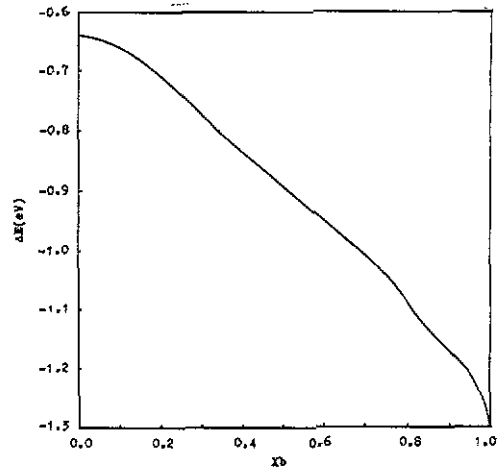
(after) chemisorption as given in [6], and the results are shown in table 2. Unlike in the case of atomic hydrogen adsorption [7], the change of the surface component concentration (see table 2) due to the chemisorption for the systems of O/Ni–Cu and CO/Ni–Cu cannot be neglected, and this drastically affects the chemisorption energy. In figure 1, the graph has a steep slope. This means that the chemisorption for the O/Ni–Cu system strongly constrains surface segregation, resulting in an enriched Ni concentration in the surface layer for all compositions and chemisorption properties more like the behaviour of O/Ni than that of O/Cu. Compared with the case in which the mutual influence of the chemisorption and surface segregation [8] need not be considered, the result is that the chemisorption energy decrease further and the chemisorption is more stable. In figure 2, the curve's shape resembles that of curve c in figure 2 of [1], which shows that the results obtained by using the ATA are as good as those obtained by using the CPA, but now a self-consistent calculation has been omitted. For the CO/Ni–Cu system, the chemisorption property is similar to that of the O/Ni–Cu system, i.e. they can all constrain surface segregation and strengthen the chemisorption. Here, we see again the result of the mutual influence of chemisorption and surface segregation.

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