Surface segregation in binary alloys

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A semiempirical calculation is outlined that allows analysis of experimental results for the apparent surface concentration of binary alloys, obtained by x-ray photoelectron spectroscopy, (XPS). A segregation profile giving the enrichment of the segregating element at and near the surface is obtained from the analysis. Using previously published data for $Cu_{17} Ni_{83}(100)$ and $Cu_{17} Ni_{83}(111)$, it is shown that copper segregation is not restricted to the first few layers, but instead extends significantly into the selvedge (near-surface) region. This occurrence is not explainable by the use of present ideal solution models. An extended ideal solution model is presented, in which the bond strengths vary gradually from top-layer values to bulk values. This model is consistent with the observed penetration of copper enrichment into the selvedge. The parameters describing the gradual change of bond strengths are determined via comparison of the results of the model with XPS data.

I. INTRODUCTION

Several semiempirical calculations[1,2] have been used recently to analyze x-ray photoelectron spectroscopy (XPS) data to ascertain the preferential segregation at the surface of one constituent of a binary alloy.[3] Electron spectroscopy signals and mean free paths have been analyzed to construct the profile of concentrations of the constituents from the surface to the selvedge to the bulk.[1,2,4-6] For the purpose of determining these profiles from XPS data, semiempirical methods have been developed for the cases in which the emission is from different core levels,[1] or from differing emission angles.[2]

These semiempirical calculations have proven to be in good agreement with more direct measurements that combine XPS and Ar^+ ion bombardment of the surface, for the case of an $Fe_{72} Cr_{28}$ alloy.[1] For this case, the methods suggest that the segregation concentration profile as a function of depth from the surface is similar to a Gaussian or exponential curve for equilibrium segregation.[1] They also indicate that segregation may occur not merely for the topmost layer of a surface, but for many atomic layers away from the surface as well.

Previous theoretical calculations imply that in most cases, significant segregation does not occur beyond a few layers below the surface. Kumar[7] and Donnelly and King[8,9] have performed these calculations for alloys of Ni–Cu, Ag–Au and Au–Pt, covering a wide range of values of bulk concentrations. In all cases, the concentration at the third layer (the top layer is defined as the first layer) differed from that of the bulk by a few percent or less.

In this communication, we shall summarize the results of the semiempirical calculations based on the XPS data, which have been reported elsewhere.[4] We shall also develop a model to explain the profiles. The analysis will be applied to previously published results on $Cu_{17} Ni_{83}(100)$ and $Cu_{17} Ni_{83}(111)$ surface segregation.[2,5,6]

II. CALCULATION OF PROFILE PARAMETERS

We restrict our discussion to miscible, substitutional alloys of the *clustering* type, i.e., those alloys for which the bond strength between unlike atoms is greater than the mean of the bond strengths of like atoms (averaged over the two components). For such alloys, the number of like-atom nearest neighbor bonds exceeds the number occurring for random location of the constituents. Kumar[7] and Donnelly and King[8] have provided evidence that Cu–Ni alloys fall into this category.

For such alloys, it is reasonable to expect that the profile will be monotonic. Any chosen profile shape (e.g., an exponentially decaying form) requires at least two characteristic parameters to be determined from XPS data: the top layer segregation δ, and the segregation depth G (in units of the layer separation d).

Let A and B denote the two elements of the binary alloy, with A being the element that segregates to the surface. (Thus, A is copper for Cu–Ni alloys.) The fraction f_i of element A for the ith atomic layer is given by

$$f_i = r + \delta e^{-i/G}, \tag{1a}$$

for the exponential profile. r is the bulk fraction for A; the top surface layer is $i = 0$. From a knowledge of f_i, the relative XPS intensity C of component A can be calculated (fixed core level and emission angle). C is the emission intensity (normalized by the differential cross sections for emission) of element A divided by the sum of the normalized intensities of A and B.

The expression for C can then be shown[4] to reduce to the result

$$C = (1 - e^{-1/\lambda}) \sum_{i=0}^{\infty} f_i e^{-i/\lambda}. \tag{2}$$

In Eq. (2), λ is the effective average mean free path (in units of d) for photoelectrons emitted from the particular core level, from the two constituents. The relation $\lambda = \lambda_0 \cos \theta$ yields λ, where λ_0 is the actual average mean free path and θ is the emission angle, relative to the surface normal.

A more accurate expression for C can be obtained by using the individual mean free paths for the two elements instead of the average.[4] However, for $Cu_{17} Ni_{83}$, the analysis showed that the approximate formula gives results that are very

close to those of the accurate analysis, and hence we shall use Eq. (2) in the following analysis.

Combining Eqs. (1a) and (2) yields the result

$$C = r + \frac{\delta(1 - e^{-1/\lambda})}{1 - e^{-1/\lambda}e^{-1/G}}. \qquad (3a)$$

In studying segregation of copper in the $Cu_{17}Ni_{83}$ alloy, XPS $2p_{3/2}$ signals were obtained for two different emission angles (45° and 75°).[5,6] This gave two different values for λ. Hence, Eq. (3a) generates two equations, corresponding to the two measured values of C.

The procedure is similar for a Gaussian profile. The form

$$f_i = r + \delta e^{-i^2/G^2} \qquad (1b)$$

replaces Eq. (1a). The expression for C analogous to Eq. (3) is

$$C = r + \delta(1 - e^{-1/\lambda}) \sum_{i=0}^{\infty} e^{-i^2/G^2} e^{-i/\lambda}. \qquad (3b)$$

Employing Eqs. (3a) and (3b), a computation of δ and G was performed[4] for the $Cu_{17}Ni_{83}(100)$ and $Cu_{17}Ni_{83}(111)$ data for samples that were annealed at 800 K to achieve equilibrium segregation and then quenched to room temperature.[5,6] The results are presented in Table I and Fig. 1, and show that segregation is not restricted to the surface, but extends into the selvedge as well. The effect of typical experimental errors was analyzed,[4] and shows that such errors do not significantly change the calculated values of G and δ.

The methods outlined so far, however, do not provide any criteria to select one particular profile shape over any other. This is because when the experiment is such as to provide only two values of C, then Eq. (3) can be solved exactly to give values of G and δ to fit the data perfectly. This suggests that XPS experiments should be performed which yield more than two data points, each corresponding to a different mean free path. Then there will be no value of G and δ which will give a perfect fit, and hence different profile shapes can be compared by the error between the calculated and experimentally observed values of C.

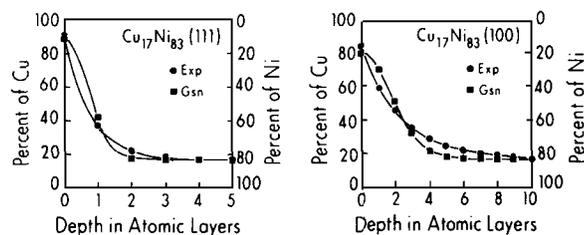Semiempirical Profiles for $Cu_{17}Ni_{83}$

FIG. 1. Segregation profiles are obtained from the semiempirical calculation, using Eq. (1) and values of δ and G obtained from the analysis of the XPS data (Table I).

III. THE MODIFIED IDEAL SOLUTION MODEL

In the theoretical work of Kumar[7] and Williams and Nason,[10] the alloy energy is taken to be the sum of the energy of the bonds between nearby atoms (generally first nearest neighbors only). The total free energy is written as the sum of the free energies over the bonds; minimizing this sum with respect to the concentration ratio in each layer, they obtain a set of equations which determine the concentration profile. The calculations of Donnelly and King[8,9] are in the same spirit, but use Monte Carlo techniques.

The contribution of elastic strain to surface segregation has been considered by Wynblatt and Ku,[11] Wynblatt and Steigerwald,[12] Abraham,[13] Abraham et al.,[14] Hamilton,[15] Miedema,[16] Kumar,[17] and Tomanek et al.[18] In experimental studies on tin–lead alloys, Frankenthal and Siconolfi[19] have shown the importance of elastic strain effects in this alloy.

For alloys of nickel–copper, a rough estimate[20] shows that the free energy of adsorption ΔQ_{el} due to elastic strains is about 10% of the free energy of adsorption ΔQ_{ϵ} due to bond breaking at the surface. Hence, we will ignore elastic strains in the subsequent discussion.

In the simple bond-breaking theories, Williams and Nason[10] have done a comprehensive study of the "ideal" and "regular" solution models. They assume that bond strengths remain the same everywhere in the crystal, except at the first layer, where they differ from the bulk values (surface relaxation). Donnelly and King[8] have assumed that the bond strengths are related to the number of nearest neighbors of an atom, and hence, the strengths differ at the surface from that in the bulk. Clustering effects (within a single layer) are accounted for by the Monte Carlo procedure. Kumar[7] has included in his analysis the tendency of like atoms to cluster together, by introducing "short range order parameters." All these approaches, however, retain the implicit assumption that the bond strengths have one value at the surface, another in the bulk, and the transition between these two is sudden and not gradual. Hence, it is not surprising that the models predict segregation only in the top few layers.

We now present a model to attempt an explanation of the gradual change in the segregation profile from the surface to the bulk. The following notation will be used:

L = number of nearest neighbors of an atom, located in the same layer; V = number of nearest neighbors of an atom in layer i, located in the layer $i + 1$; $a_i (b_i)$ = enthalpy of the A–A, (B–B) bond when both atoms are in the ith layer; x_i

TABLE I. Profile parameters for $Cu_{17}Ni_{83}$ (single mean free path approximation).

Parameter	$Cu_{17}Ni_{83}(111)$	$Cu_{17}Ni_{83}(100)$
λ = average mean free path in atomic layers		
45° emission	2.70	3.10
75° emission	0.99	1.10
C_{Cu} = fractional Cu signal		
45° emission	0.45	0.52
75° emission	0.69	0.71
Exponential profile parameters segregation depth G		
(atomic layers)	0.756	2.272
top layer segregation δ	0.739	0.675
Gaussian profile parameters		
G (atomic layers)	0.984	2.501
δ	0.724	0.630

= enthalpy of the A–B bond when both atoms are in the ith layer; H = total enthalpy of mixing for the alloy.

We make the following assumptions:

(1) The two constituents occupy the lattice sites randomly. This assumption does introduce some small errors, as nickel–copper alloys are found to be weakly clustering.[7,8] However, the analysis that follows could easily be generalized to include clustering.

(2) The enthalpy of a bond between an atom in the ith layer and one is the $(i + 1)^{th}$ layer is the same as that between two atoms in the ith layer. This assumption does simplify the analysis considerably and the error introduced is small. Only nearest neighbor bonds are considered.

(3) The alloy is an "ideal solution", which means that

$$x_i = (a_i + b_i)/2. \qquad (4)$$

We estimate the error in this assumption as less than 15% for the Cu–Ni alloy under consideration.[21]

(4) The surface relaxation described by Williams and Nason[10] is not abrupt, but rather the bond strengths change slowly from the surface to the bulk. In view of the expectation that the resulting profiles may be close to that of an exponential or Gaussian, we may assume a similar functional form for the bond strengths. For an exponential form choice,

$$a_i = a + \alpha e^{-i/g}, \qquad (5a)$$

$$b_i = b + \beta e^{-i/g}. \qquad (5b)$$

Here, a and b are the bulk values for the bond enthalpies, α and β are the surface relaxation parameters determining the change in the enthalpy between top layer and bulk. Also, g is the decay constant. We have assumed that the value of g is the same for both types of bonds.

The following analysis resembles that of Williams and Nason.[10] The total enthalpy is

$$H = \sum_{i=0}^{\infty} \left\{ \frac{L}{2}[f_i^2 a_i + 2f_i(1 - f_i)x_i + (1 - f_i)^2 b_i] \right.$$

$$+ V\{f_i f_{i+1} a_i + f_i(1 - f_{i+1})x_i$$

$$\left. + (1 - f_i)f_{i+1} x_i + (1 - f_i)(1 - f_{i+1})b_i\} \right\}. \qquad (6)$$

The total entropy is given by

$$S = -\sum_i kf_i \ln f_i - \sum_i k(1 - f_i)\ln(1 - f_i) - \sum_i \phi kf_i, \qquad (7)$$

where k is Boltzmann's constant and ϕ is a constant independent of f_i. The free energy F is given by $F = H - TS$. This can be minimized with respect to the concentrations f_i to yield a system of equations for f_i. The results are

$$\partial F / \partial f_i = L(x_i - b_i) + Lf_i(a_i + b_i - 2x_i)$$

$$+ Vf_{i+1}(a_i + b_i - 2x_i)$$

$$+ Vf_{i-1}(a_{i-1} + b_{i-1} - 2x_{i-1})$$

$$+ V(x_i - b_i) + V(x_{i-1} - b_{i-1})$$

$$+ kT \ln[(f_i)/(1 - f_i)] + \phi kT = 0. \qquad (8)$$

This can be simplified by using Eq. (4) and by defining θ_i

= $(a_i - b_i)/2kT$, $\theta = (a - b)/2kT$ and $\gamma = (\alpha - \beta)/2kT$, so that $\theta_i = \theta + \gamma e^{-i/g}$. The result is

$$L\theta_i + V\theta_i + V\theta_{i-1} + kT \ln[f_i/(1 - f_i)] + \phi kT = 0, \qquad (9a)$$

$$L\theta + 2V\theta + kT \ln[(r/(1 - r)] + \phi kT = 0. \qquad (9b)$$

In Eqs. (8) and (9a), f_{i-1} and θ_{i-1} are defined as zero for $i = 0$. Equation (9b) expresses the fact that the bulk concentrations apply for $i \rightarrow \infty$. This equation can be used to eliminate ϕ by defining

$$Y_i = \frac{f_i/(1 - f_i)}{r/(1 - r)}. \qquad (10)$$

Subtracting Eq. (9b) from (9a) then yields

$$(L + V)(\theta_i - \theta) + V(\theta_{i-1} - \theta) + kT \ln Y_i = 0. \qquad (11)$$

Thus, the concentration profile is given by

$$f_i = \frac{rY_i/(1 - r)}{1 + rY_i/(1 - r)}, \qquad (12)$$

with the Y_i's computable from Eq. (11).

This yields expressions for the f_i's in terms of three parameters-θ, γ, and g, for each of the chosen profile shapes (exponential, Gaussian, etc.). In terms of these f_i's, we can calculate the values of C from Eq. (2). As in the previous work,[4] we introduce the error parameter

$$\epsilon = \sum[C_{expt} - C(\gamma,\theta,g)]^2, \qquad (13)$$

where the sum is over the four different values of C corresponding to the two different surfaces and the two emission angles, from the data of Refs. 5 and 6. Then, ϵ can be minimized with respect to γ, θ, and g to yield the best fit values for these parameters. The minimum value of ϵ thus obtained is an indication of the degree of fit, and different profile shapes can be compared to each other on basis of the value of ϵ_{min}. This calculation was performed for $Cu_{17} Ni_{83}$ and the results are presented in Table II.

IV. DERIVATION OF θ, γ, AND g FROM EMPIRICAL DATA

It is possible to get expressions for θ, γ, and g from data other than that of XPS. This gives us independent estimates of these parameters which can be compared with those obtained by the preceding approach.

The heats of vaporization of the individual pure elements give a direct measure of θ. This can be seen by noting that θ is half the difference in the bulk values of the A–A and B–B bond enthalpies in units of kT. Let us assume that the enthalpy in the alloy has the same value as in the pure crystal. Letting Z be the total number of nearest neighbors of a bulk atom, we obtain the result $(\Delta H_V)_A = (Z/2)a$ for the heat of vaporization per atom $(\Delta H_V)_A$ of pure solid A, and an analogous equation for $(\Delta H_V)_B$. Thus, from its definition,

$$\theta = [(\Delta H_v)_B - (\Delta H_V)_A](1/ZkT). \qquad (14)$$

A second empirical relation is obtained from the energy required to cleave the crystal along a particular plane. Let τ_A, τ_B be defined by letting $\tau_A d_A^2$ and $\tau_B d_B^2$ denote the cleaving energy per atom for pure crystals of A and B, re-

TABLE II. Calculations of parameters for $Cu_{17}Ni_{83}$ at $T = 800$ K.

(a) Parameters from minimization of the error parameter ϵ in Eq. (13)

$A = Cu, B = Ni$
$L(100) = 4, L(111) = 6$
$V(100) = 4, V(111) = 3$

Results	Exponential	Gaussian
$\theta = (a - b)/2kT$	0.847	0.815
$\gamma = (\alpha - \beta)/2kT$	-0.109	-0.107
Relaxation depth g (atomic layers)	5.143	4.022
Error ϵ_{min}	2.865×10^{-3}	2.850×10^{-3}

(b) Parameters obtained from other empirical data

Heats of vaporization

$(\Delta H_V)_{Cu} = 80.014$ kcal/mol
$(\Delta H_V)_{Ni} = 102.054$ kcal/mol

Energy to cleave crystal along (100) plane

$\tau_{Cu} = 1.660$ J/m^2
$\tau_{Ni} = 2.133$ J/m^2

Nearest neighbor separation in pure crystals

$d_{Cu} = 3.615 \times 10^{-10}$ m
$d_{Ni} = 3.524 \times 10^{-10}$ m.

Results: $\theta = 1.157$, $\gamma = -0.189$

The value of θ is obtained from Eq. (14). The value of γ is obtained from Eq. (16), using the values of g taken from part (a) of this table.

spectively, where d_A, d_B denote the corresponding nearest neighbor separations. The energy of cleaving arises partly in breaking V bulk bonds/atom, and partly in the creation of two new surfaces. Thus we can write

$$-\tau_A d_A^2 = Va + 2[(L/2) + V] \sum_{i=0}^{\infty} (a - a_i) \quad (15a)$$

and

$$-\tau_B d_B^2 = Vb + 2[(L/2) + V/] \sum_{i=0}^{\infty} (b - b_i). \quad (15b)$$

For the exponential form, Eq. (5), this yields

$$(1/kT)[\tau_A d_A^2 - \tau_B d_B^2]$$

$$= -2V\theta + 4[(L/2) + V] \sum_{i=0}^{\infty} \gamma e^{-i/g}$$

$$= -2V\theta = 4[(L/2) + V]\gamma/(1 - e^{-1/g}). \quad (16a)$$

Choosing a Gaussian form, i.e., replacing i by i^2 in the exponents of Eq. (5), yields

$$(1/kT)[\tau_A d_A^2 - \tau_B dd_B^2]$$

$$= -2V\theta + 4[(L/2) + V]\gamma \sum_{i=0}^{\infty} e^{-i^2/g^2}. \quad (16b)$$

The values for ΔH_V, τ and d for the two elements were obtained from references listed in Donnelly and King.[8] θ was calculated from Eq. (14). Eqs. (16) contain both γ and g, but it can be seen from inspection of Eq. (16a), for example, that for values of g of the order of those in Table II, the results are not sensitive to g. Hence, we solved Eqs. (16) using the values of g from Table II(a), and obtained a result

for γ, choosing the exponential profile relation Eq. (16a). These results are presented in Table II(b).

V. DISCUSSION

Figure 1 shows the profiles resulting from the semiempirical calculation, using Eq. (1) and values for δ and G obtained from the analysis of the XPS data. We see that segregation is not restricted to the top layer, but that the concentration profile varies gradually from the surface through the selvedge to the bulk. This implies the need of a model that predicts a gradual segregation, so that models which begin by restricting the surface relaxation to the topmost layer are inadequate for this purpose.

In Table II(a), we have calculated the parameters of our extended ideal solution model, by minimizing the error parameter ϵ defined by Eq. (13). The employed energy profile, i.e., the variation of the bond strength with depth from the surface, is plotted in Fig. 2 for both exponential and Gaussian forms. Using these forms, and Eqs. (11) and (12), we can compute the segregation concentration profiles predicted by the model. The results are presented in Fig. 3, using the results for θ and γ computed in Table IIb. It is seen that the segregation profiles are similar in shape to the energy profiles, in that (except for the topmost layer), they have the exponential or Gaussian shape assumed for the energy profiles. The substantial difference at the top layer is due to the different form for the expression for the first layer concentration Y_0 [Eq. (11)] as compared to the form for Y_i for $i > 0$. In the form for Y_0 ($i = 0$) the term θ_{i-1} must be set to zero. Y_i directly determines f_i via Eq. (12). In physical terms, this variation occurs due to the absence of a layer above the topmost layer.

This large segregation at the topmost layer is seen to occur even in absence of surface bond relaxation ($\gamma = 0$), as has been discussed by Williams and Nason.[10] The segregation in the lower layers is caused in our model solely by the gradual

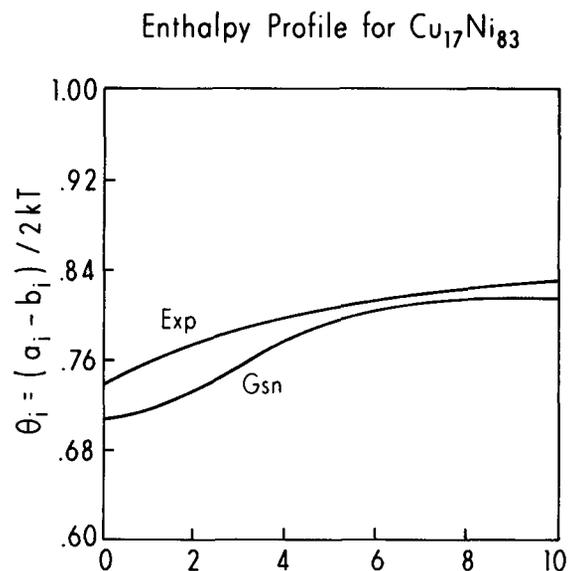Enthalpy Profile for $Cu_{17}Ni_{83}$

FIG. 2. Enthalpy profile is given for the exponential and Gaussian forms. For the exponential form, Eq. (5) is employed, while the Gaussian form is derived from Eq. (5) after replacement of i by i^2.
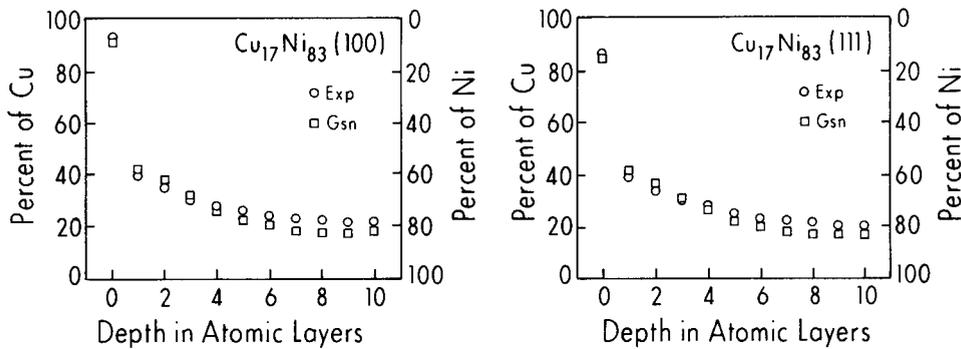
Concentration Profiles for $Cu_{17}Ni_{83}$ from Ideal Solution Model

FIG. 3. Concentration profiles f_i are given by Eq. (12). The values of Y_i are found from Eq. (11). The shape of the concentration for the energy profile is similar to that assumed for the energy profiles (exponential or Gaussian) except for the significantly increased segregation at the first layer ($i = 0$). This derives from the absence of a layer above the top layer.

change in the surface bond relaxation.

Despite the fact that the ideal solution model we have developed gives values for the parameters that are independent of the surface chosen [(100) or (111)], the resulting profiles are different for the two surfaces, as seen in Fig. 3. This is due to the fact that the values of L and V are not the same, for the two surfaces.

As can be seen from Fig. 3, the top layer segregation δ for $Cu_{17}Ni_{83}$ obtained from this model is greater for the (100) surface than for the (111) surface. This differs from the results of the semiempirical calculation (Table I and Fig. 1), which yield δ larger for the (111) surface. The ideal solution results, however, are compatible with our expectations. Since the (100) surface is loosely packed, relative to the (111) surface, it is reasonable that the segregation is greater for the (100) surface.[22] Thus the present model (which does not impose a particular analytic form for the concentration profile) does appear to be an improvement over the semiempirical calculation, as the latter yielded counter-intuitive results when δ for the (100) surface is compared with δ for the (111) surface.

Reasonably good agreement is obtained between the values of θ and γ obtained from our model [Table II(b)], and those obtained from XPS empirical data, [Table II(a)]. This seems to indicate that the model is reasonably accurate in describing segregation in $Cu_{17}Ni_{83}$, though its results are yet to be tested on a wide variety of samples.

The values of ϵ_{min} for exponential and Gaussian forms (Table II) suggests that the Gaussian form is more accurate, but the difference is not substantial. More data need to be taken for the model to be tested rigorously.

In summary, we find that the current models for segregation do not satisfactorily explain the data[5,6] of the experimentally determined segregation profiles. A theoretical model which predicts a gradual segregation concentration profile is necessary to explain the equilibrium surface segregation. We propose a model where the bond enthalpies gradually change from the surface to the bulk as one method of explaining existing semiempirical results[2,4] for the segregation profile for $Cu_{17}Ni_{83}$.

In this work we have not included the effects of clustering (nonrandomness in the distribution of alloy components),[7,8] or extended the analysis to regular solutions.[7,8,10] The fairly close agreement of our results for θ, γ from fitting of segregation data [Table II(a)] with their values from other data [Table II(b)] indicates that these assumptions are reasona-

ble in a first analysis that employs a gradual decay of the bond strengths from surface to bulk. We have tried to show that better theoretical models of segregation are possible and that more work in this area is indicated.

Note added in proof: Forward scattering of the type described by W. Egelhoff[23] may affect semiempirical determinations of surface segregation of the type described here. The results reported here are not, however, believed to be significantly affected by forward scattering due to the large acceptance angle of the electron energy analyzer with which the original data were acquired (See Refs. 5 and 6).

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[20]To estimate the ratio $|\Delta Q_{el}/\Delta Q_e|$, we have used Eqs. (3.4), (3.11), and (3.12) of Ref. 3 for the (100) surface of a nickel–copper alloy. For nearest neighbor interactions represented by a Lennard-Jones 8 − 4 potential, the result for the ratio is 0.096. The elastic strain contribution is small because the ratio r_{Ni}/r_{Cu} of atomic radii is 1.03, corresponding to very little size mismatch.

[21]To estimate the error in the assumption that Ni–Cu is an ideal solution [as in Eq. (4)], we define $\Omega = [(a + b)/2] - x$ and let $\Omega/\theta kT$ be a measure of the deviation of the actual alloy from the ideal case. In Refs. 8 and 10, the estimates for Ω yield values for $\Omega/\theta kT$ equal to 0.14 and 0.12, respectively. This indicates a possible error of about 15% in the assumption of an ideal solution.

[22]That the top layer segregation should be greater on the more open (100) face is exhibited by noting that $\Delta z(100) = 4$, while $\Delta z(111) = 3$. Here, Δz is the difference in coordination number between a bulk site and a surface site.

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