Thermochemical Values for Cu-Ni Surface and Interface Segregation Deduced from Core-Level Binding-Energy Shifts

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A new method for extracting thermochemical values of surface and interface segregation in binary alloys from shifts in core-electron binding energies is applied to the case of Cu-Ni. The results for the heat of Cu surface segregation agree well with the calculated value. In addition to providing important thermochemical values this approach provides new insights into the relative importance of the different effects contributing to segregation phenomena.

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As binary alloys have become increasingly important technologically, the need for an understanding of the surface and interface thermodynamics of these materials has become vital.[1] Surface and interface segregation often occur in binary alloys, but so far, determination of the heats of surface and interface segregation has been very difficult. This is largely due to the difficulty of making accurate measurements of the surface and interface elemental concentrations and to the need to make the ideal-solution approximation. Thus the need for a better approach is clear. It was recently demonstrated by Rosengren, Johansson, and Mårtenson[2] that, at least for surface segregation, a better approach would be to use shifts in core-level binding energy and the equivalent-core approximation in a Born-Haber cycle analysis to extract heats of surface segregation.

The purpose of the present work is, first, to demonstrate that the rather cumbersome Born-Haber cycle part of the analysis can be replaced by a new, much simpler conceptual framework which is easier to understand and apply; second, to demonstrate that the approach may be applied to the as yet untreated case of determining a heat of segregation into a metallic overlayer; third, to present the first measurement of the surface core-level shift (SCLS) in Ni; fourth, to demonstrate that the approach may be applied to the as yet untreated case of determining a heat of interface segregation; fifth, to show how the new insights provided here make possible a new approach to separating out the fundamental driving forces in surface and interface segregation; and sixth, to point out that the thermochemical quantities determined for the overlayer and interface cases cannot, at present, be determined by any other method.

Figure 1 illustrates the conceptual framework which relates core-level binding-energy shifts to thermochemical quantities. This approach uses, as did earlier work,[2] the equivalent-core approximation. The equivalent-core approximation is an excellent approach for estimating the physical-chemical properties of an atom containing a fully screened core hole by simply equating it to the next element in the periodic table (i.e., $Z+1$).[3,4] This approximation is used in Fig. 1 to equate the final state (a Ni atom with a fully screened core hole) with a Cu atom, and is represented in Fig. 1 by filled circles. Figure 1 thus consists of a single initial state [a Ni(100) sample] and two possible final states, one in which x-ray photoelectron spectroscopy (XPS) creates a core hole on a bulk Ni atom and one in which XPS creates a core hole on a surface Ni atom. Since there is only one initial state, the difference in the measured core-level binding energies, ΔE_b, corre-

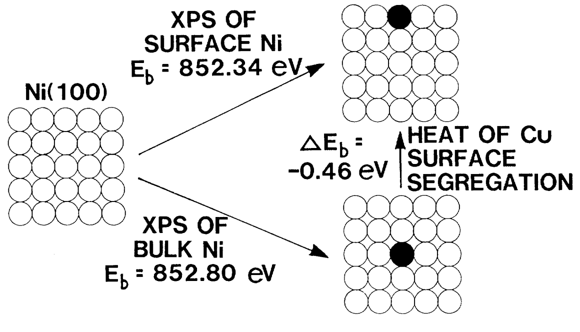

FIG. 1. An illustration of the single initial state and the two possible final states which, together with the equivalent-core approximation, relate the surface core-level shift to the heat of surface segregation of Cu in Ni. Open circles represent Ni atoms, and closed circles the equivalent-core version of Cu atoms.

sponds to the difference in energy between the two final states. When the equivalent-core approximation is made for these two final states, this binding-energy difference is the energy difference between a Cu atom in the bulk and a Cu atom at the surface. This, in turn, is just the heat of surface segregation. Thus Fig. 1 makes the relationship between core-level binding-energy shifts and the heat of surface segregation an easily grasped concept and avoids resorting to the more complex Born-Haber cycle analysis.[2] It should be noted that this approach, while it works best for elements adjacent in the periodic table, can be extended to cover a wide range of binary alloys.

The values for E_b in Fig. 1 are determined in the present work and represent the first SCLS determination for Ni.[5] The method for separating the bulk and surface core-level peaks in the XPS of Ni(100) is based on the difference between two spectra. One is that of the clean Ni(100) surface, and the other is that of the Ni(100) surface with several monolayers of another metal epitaxially deposited on it. Results for this procedure are presented in Fig. 2 for the case of four monolayers of Co deposited on the Ni(100) surface. The Ni $2p_{3/2}$ core level is selected for study, first, because it is a deep core hole, thus making it ideal for the equivalent-core approximation; and second, because in XPS it is the narrowest Ni core level, thus making it best for separating closely spaced peaks. For the data in Fig. 2, the normalization of the four-monolayer Co + Ni(100) spectrum prior to subtraction from the clean Ni(100) spectrum is based on the fact that if the four monolayers of Co substantially shift the surface Ni core-level peak, then the difference intensity remaining after the subtraction must equal the intensity from the surface Ni layer. This intensity was separately determined for the present instrument by careful epitaxial deposition of exactly one monolayer of Ni on Cu (100). The difference intensity from this procedure would exhibit an unshifted peak if there were no SCLS or if the four monolayers of Co failed to shift the surface core level substantially. However, as seen in Fig. 2, the difference peak is not only substantially shifted but, in fact, has the same shape and width as the four-monolayer Co + Ni(100) peak. This is powerful evidence that the four-monolayer Co overlayer shifts the surface Ni core-level peak to the bulk position. This indicates that the SCLS for Ni(100) is $\Delta E_b = -0.46$ eV. The same procedure using Cr, Mn, and Fe overlayers yields $\Delta E_b = -0.43$, -0.44, and -0.51 eV, respectively. A similar procedure also works for saturating the Ni(100) surface with CO molecules. However, in this case, the surface peak is shifted even more, going slightly beyond the bulk peak position.[6] If we take the average of the Cr, Mn, Fe, and Co overlayer results, the value determined for the heat of Cu segregation to a Ni(100) surface is -0.46 eV ($= -10.6$ kcal/mole). The minus sign means that the process is exothermic. It is also noteworthy that the value of this quantity has been calculated theoretically by Miedema to be -8.5 kcal/mole,[7] in good agreement with the present result.

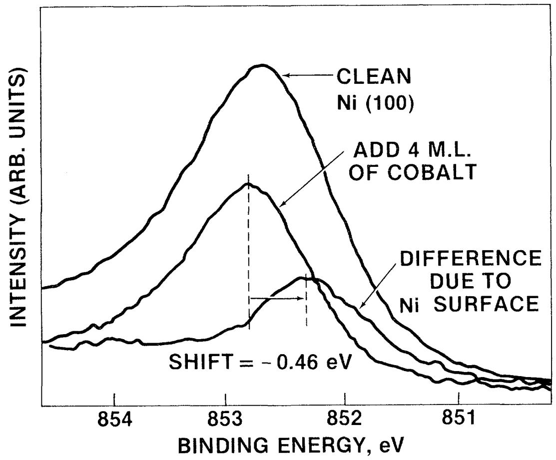

FIG. 2. X-ray photoelectron spectra of the Ni $2p_{3/2}$ core level for the clean Ni(100) surface, the Ni(100) surface covered by four epitaxial layers of Co, and the difference between these two spectra.

A deeper understanding of segregation phenomena can be obtained by considering some other results. By use of the same general approach as above, data from an epitaxial Ni monolayer on Cu(100) have been analyzed. The analysis is analogous to that of Fig. 1 but adapted[8] for this different situation, and produces the relationship that the heat of Cu surface segregation into the Ni overlayer (exchange of a bulk Cu atom with a surface Ni atom) equals the difference in the Ni core-level binding energy between the Ni overlayer and an isolated Ni atom in bulk Cu. The measured ΔE_b for this case, -0.07 eV ($= -1.6$ kcal/mole), is thus the heat of Cu surface segregation into the Ni overlayer. Note that this quantity cannot, at present, be determined by any other method.

It may at first seem surprising that the heat of surface segregation values of -10.6 and -1.6

kcal/mole differ so widely. However, upon closer examination, the reason for this becomes very clear and leads to new, interesting, and important insights into the relationships between alloy thermochemistry, XPS, and surface segregation.

To see this, it should first be noted that for both Cu in Ni and Ni in Cu, the heat of solution is endothermic.[9] This has a major influence on the heats of surface segregation. In the case of Cu in Ni (Fig. 1), Cu dissolves in Ni endothermically so that this potential energy is available to help drive surface segregation by contributing to the value of −10.6 kcal/mole. In contrast, for the Ni monolayer on Cu, a Ni atom must be dissolved (endothermically) in Cu for a Cu atom to come out to the surface, and this acts in opposition to Cu surface segregation, producing the small value of −1.6 kcal/mole. Since the heat of surface segregation depends both on heats of solution and on surface free energies,[7] what is needed here is to separate the contributions.

To do this, it is useful to compare the E_b value for the Ni monolayer on Cu with the value for the clean Ni(100) surface (viz., a Ni monolayer on Ni). The experimental result, $\Delta E_b = 0.0 \pm 0.02$ eV, together with the equivalent-core approximation, shows directly that the change in energy upon replacing a Ni atom with a Cu atom in a surface Ni monolayer is very nearly independent of whether the Ni monolayer is supported by Cu or Ni. This is a very important point since it means that the surface-energy contribution to surface segregation does not depend on the identity of the nearest-neighbor atoms at the surface site which is involved in segregation. This being the case, a good approximation to the surface-energy contribution will be just the difference in surface energy, σ, between Cu and Ni which, expressed in terms of (100) surface atoms, is $\sigma_{\mathrm{Cu}} - \sigma_{\mathrm{Ni}} = -3.3$ kcal/mole.[7] Since this is the surface-energy contribution to both heats of surface segregation (−10.6 and −1.6 kcal/mole), it follows that the heat of solution of Ni in Cu in the infinite-Ni-dilution ($[\mathrm{Ni}] \to 0$) must be +1.7 kcal/mole,[4] which is the amount by which −3.3 kcal/mole is reduced to get the observed value of −1.6 kcal/mole. Likewise, for Cu in Ni (at $[\mathrm{Cu}] \to 0$) the heat of solution must be +7.3 kcal/mole,[4] which is the amount by which −3.3 kcal/mole is increased to get the observed value of −10.6 kcal/mole.

This separation of contributions provides several new insights. The most obvious is that for Cu (at $[\mathrm{Cu}] \to 0$) the heat of solution of Cu in Ni (+7.3 kcal/mole) is more than twice as large a contribution to the heat of surface segregation as the surface-energy contribution. This is particularly significant since for most binary alloys, including Cu-Ni, the heat of solution values change markedly with concentration. For Cu-Ni, the heat of solution of Cu in Ni rises sharply as $[\mathrm{Cu}] \to 0$.[9] This means that the heat of Cu surface segregation will become appreciably more exothermic in the $[\mathrm{Cu}] \to 0$ limit. Strong support for such a change comes from existing data on Cu-Ni alloys, which suggests a heat of Cu surface segregation of roughly −5 kcal/mole for compositions between 10.7% and 52% Cu (Ref. 10); as expected, this value is quite different from the present value of −10.6 kcal/mole in the $[\mathrm{Cu}] \to 0$ limit. In this context it is clear that XPS is uniquely well suited to determinations of heats of surface segregation in the zero-concentration limit. Moreover, the present work indicates that heats of surface segregation can be predicted for Cu-Ni alloys over the whole range of concentration by the relatively simple approach of combining the appropriate heat-of-solution values (see Ref. 9) with the surface-energy contribution of −3.3 kcal/mole.

The general approach of the present work is readily applicable to the problem of determining heats of interface segregation. This can be illustrated for the case of Cu in Ni segregating to a Cu(100)-Ni(100) interface. It might be anticipated that since the heat of solution of Cu in Ni rises sharply for $[\mathrm{Cu}] \to 0$, Cu would segregate to the interface and thus acquire more Cu nearest neighbors. This is indeed the case and is demonstrated by depositing epitaxial layers of Cu on Ni(100) and measuring E_b for the top Ni layer. The analysis is just as in Fig. 1 except that there are several epitaxial overlayers of Cu on Ni(100) in both the initial and final states. The experimental value of ΔE_b (Ni at the interface − bulk Ni) = −0.31 eV (= −7.1 kcal/mole) corresponds to the heat of segregation of Cu to the Cu-Ni interface. Again, this quantity cannot, at present, be determined by any other method. It is noteworthy that this value is almost exactly equal to the negative of the heat of solution of Cu in Ni in the $[\mathrm{Cu}] \to 0$ limit, determined above to be +7.3 kcal/mole. This means that the Cu heat of solution in Ni (strongly endothermic) essentially accounts for the entire (strongly exothermic) heat of interface segregation. Thus it is seen that for both surface and interface segregation in Cu-Ni alloys at $[\mathrm{Cu}] \to 0$ the dominant contribution comes from the heat of solution.

In summary, the present work demonstrates that XPS can determine thermochemical values that are often inaccessible by any other method and provides important, new quantitative insights into the fundamental driving forces in surface and interface segregation.

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[4] Preliminary indications are that the accuracy attainable by this general approach to determining thermochemical values is about ± 1.0 kcal/mole. See P. Steiner and S. Hüfner, Solid State Commun. 37, 79 (1981), for the accuracy of this method in bulk Pd-Ag alloys. It must be kept in mind that the excited Ni atom and the Cu atom are equated only in the sense that they are expected to have essentially indistinguishable thermochemical properties. The excellence of this approximation when used in this manner no doubt derives from the fact that the Coulomb integral for a valence-shell electron with a core electron scarcely changes when the core-electron orbital is shrunk to a point [see J. B. Mann, Los Alamos Scientific Laboratory Report No. LA-3690, 1967 (unpublished) and Ref. 3]. A more complete analysis of the anticipated error in the equivalent-core approximation is now in progress (W. F. Egelhoff, Jr., to be published). It suggests that in Cu-Ni this error makes the measured thermochemical values about 3% too small. Thus the uncertainty will depend almost entirely on the degree to which XPS can be used to determine shifts in the binding energy of the fully screened core hole.

[5] For experimental details see W. F. Egelhoff, Jr., Appl. Surf. Sci. 11/12, 761 (1982).

[6] W. F. Egelhoff, Jr., to be published.

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Universality in the Critical Broadening of Spectral Lines in Simple Fluids

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Nonlinear mode-coupling hydrodynamics is used to study the broadening of spectral lines near a liquid-gas critical point. The critical contribution to the line shape is given by a universal line-shape function. For values of $\epsilon = |(T-T_c)/T_c|$ which are not too small, the line assumes a Lorentzian form and the width $\hat{\Gamma}$ increases as $\sim \epsilon^s$ with the critical exponent $s = \gamma + \nu = -0.607$. Very close to the critical point the line changes into a Levy distribution [the Fourier transform of $\exp(-t^r)$ where $r = (3-\eta)/2$] and the line shape becomes independent of ϵ ($s = 0$).

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In this work we consider the broadening of an isolated spectral line in a fluid near a critical point. Using hydrodynamic mode-coupling techniques, we derive a universal line-shape function and analyze the critical exponent associated with the line width. Our theory accounts quantitatively for the available experimental data on vibrational dephasing in N_2 and O_2.[1] A similar model was de-