Oscillatory segregation at a metal alloy surface: Relation to ordered bulk phases

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Some transition-metal alloys exhibit a complex surface segregation, where the composition oscillates with depth. Here, such behavior is predicted to occur for CuAu(100), based on Monte Carlo calculations using an empirical classical potential for multicomponent systems. A simple model shows that this behavior is related to the existence of an ordered phase in the bulk phase diagram, with the depth of the segregation diverging at the bulk ordering temperature. This accords with the observed behavior of PtNi, which has a phase diagram similar to CuAu. The role of surface orientation is discussed, as is the related nonoscillatory surface segregation of alloys exhibiting a bulk miscibility gap.

Segregation at metal alloy surfaces is a familiar and important issue in metallurgy and in catalytic chemistry. It has long been recognized that the surface layer becomes enriched with whichever species lowers the surface energy. Recently, it has become possible to measure the composition layer by layer, using atom-probe techniques or low-energy electron diffraction. In this way, PtNi and PtRh have been observed to exhibit a more complex segregation behavior, with the composition oscillating from layer to layer with depth.^{1,2}

No explicit mechanism has to my knowledge been proposed to explain this fascinating behavior, although composition oscillations have been reproduced in mean-field calculations for PtNi.³ Here we describe Monte Carlo simulations of a CuAu(100) surface, along with a model analysis, which suggest the following extremely simple explanation.

CuAu (like PtNi) forms an ordered phase at low temperature, consisting of alternating (100) layers of Cu-rich or Au-rich composition on the underlying fcc lattice. This ordering can be readily understood as due to a preference for unlike bonds, i.e., for having Cu-Au bonds rather than Cu-Cu and Au-Au. When Au segregates to the first layer to lower the surface energy, the second layer becomes particularly favorable for Cu atoms, since they will have an enhanced number of Cu—Au bonds. This in turn favors Au in the third layer, and so on. Such an obvious explanation has no doubt been offered before; but I have been unable to locate in the literature any explicit such suggestion, or any allusion to the connection between oscillatory segregation and ordered bulk phases. In particular, the implications for the temperature dependence have apparently not been appreciated.

Clearly the strength of any oscillatory segregation should decrease with increasing temperature. However, the dependence of the *depth* of the oscillations on temperature provides a crucial test of the driving mechanism. For example, in a recent study of a SiGe alloy surface,⁴ the driving force for oscillatory segregation came from surface stresses associated with specific layers; therefore the depth was determined by the stress field, and not by the temperature. It has similarly been suggested that oscillatory segregation in metals might be driven by the oscillatory relaxation at metal surfaces, which again has a specific and limited depth.¹

In contrast, as discussed below, the mechanism suggested here implies that the depth of the oscillations should increase with decreasing temperature, in principle diverging at a critical temperature. The Monte Carlo simulations clearly show this behavior, supporting the connection between oscillatory segregation and bulk ordering. In addition, a simple expression is derived for the depth of the oscillations as a function of temperature, which demonstrates the extreme sensitivity to temperature and to surface orientation. In particular, the oscillations are predicted to go much deeper for the (100) surface than for the (111).

The method used here to study surface segregation is a type of Monte Carlo simulation, used previously by Foiles⁵ and by Kelires and Tersoff.⁴ The simulation includes small random atomic displacements, as well as moves which interchange Cu and Au atoms, allowing local compositional equilibration. The total sample composition is fixed here. An equilibrium distribution at a specified temperature is obtained in the usual way, accepting trial moves according to the Metropolis criterion.⁴

An empirical interatomic potential⁶ is used to calculate the energy at each step. This potential has been used with considerable success for semiconductors, where the parameters in the potential were fitted to the known energies of several real and hypothetical polymorphs. Unfortunately, for metals far less data is available. In fact, the choice of studying CuAu here rather than NiPt was determined by the greater availability of data for CuAu, including enthalpies of ordered phases, and vacancy formation energies in the pure metals.

Because of the dearth of data, the potential of Ref. 6 is further simplified by arbitrarily specifying certain parameters.⁷ The result, a special case of the more general potential, is

$$E = \frac{1}{2} \sum_{i \neq j} [f_R(r_{ij}) + b_{ij} f_A(r_{ij})] ; \qquad (1a)$$

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$$f_{R}(r_{ij}) = A_{ij} \exp(-2\mu_{ij}r_{ij}) ,$$

$$f_{A}(r_{ij}) = -B_{ij} \exp(-\mu_{ij}r_{ij}) ,$$

$$b_{ij} = \chi_{ij} [1 + \beta_{i}(z_{i} - 1)]^{-1/2} .$$
(1b)

Here *i*, *j*, and *k* label the atoms of the system, and r_{ij} is the length of the *ij* bond. Doubly subscripted parameters are determined from the elemental ones by the interpolation scheme⁶ $\mu_{ij} = (\mu_i + \mu_j)/2$, $A_{ij} = (A_i A_j)^{1/2}$, and $B_{ij} = (B_i B_j)^{1/2}$. Singly subscripted parameters, such as μ_i and β_i , depend only on the type of atom (Cu or Au). The atom sum is restricted to first neighbors, and z_i is the number of neighbors of atom *i* (e.g., 12 in the bulk of this fcc alloy).

This simplified form reduces the number of parameters to four per element. These suffice to fit the cohesive energy, lattice constant, and bulk modulus of the fcc crystal, and the vacancy formation energy, to any desired precision. The additional parameter χ_{CuAu} is fitted to the enthalpy of the ordered CuAu alloy; $\chi_{11} = \chi_{22} = 1$.

This potential is extremely simple and short-ranged. In fact, it is equivalent to a nearest-neighbor Morse potential, but with the parameters of the pair interaction depending upon the number as well as the type of neighbors. Thus the accuracy may be less than that of the widely used embedded-atom method.⁵ The advantages of the present approach are its extreme simplicity, and its ability to generate a rather reasonable potential with a bare minimum of input data. The most severe problem noted with the potential here was that the shear elastic constants c_{44} for Cu and Au were roughly a factor of 2 too large.

The most important properties of the alloy appear to be well described here. Table I shows the calculated enthalpy of mixing, atomic volume, and bulk modulus for the series of ordered alloys, compared with experiment.⁸ The volumes are all accurate to within 5%, equivalent to a lattice constant accuracy better than 2%. These are much more accurate overall than Vegard's law, which predicts a linear variation in lattice constant with composition. The bulk moduli and enthalpies of mixing are also well described, with errors of no more than 4% each. The latter is given twice as accurately as by regular solution theory.

The results of the Monte Carlo simulations are summarized in Fig. 1, which shows the layer-by-layer composition in equilibrium, calculated for a CuAu(100) surface. The simulation cell used here is a 15-layer (100) slab, with

TABLE I. Enthalpy of mixing ΔH (meV/atom), bulk modulus *B* (GPa), and volume *V* (Å³ per atom), for ordered CuAu alloys, calculated with the present potential. Experimental data of Ref. 8 are given in parentheses.

	ΔH	В	V
Cu		137 (138)	11.7 (11.8)
Cu₃Au	-71(-74)	148 (148)	13.1 (13.8)
CuAu	-91(-91)	157 (163)	14.4 (14.5)
CuAu ₃	-46	162	15.8 (15.8)
Au		169 (171)	17.0 (17.0)



FIG. 1. Calculated alloy composition for each layer at the CuAu(100) surface. Temperatures are indicated. Note that layer 8 is the center layer of the 15-layer slab.

270 atoms per cell (18 per layer) periodically repeated in two dimensions. [The (111) surface is discussed below.]

One obvious effect in Fig. 1 is the strong segregation of Au to the surface. Au has a lower surface energy than Cu, about 0.12 eV/atom lower for the (100) surface with this potential. (Experimental surface energies of metal crystals are unfortunately not available.) However, the feature of most interest here is that the Au concentration is strongly *reduced* in the second layer, relative to the bulk. Thus the concentration profile at the surface is predicted to oscillate, as in the case of PtNi or PtRh.

At a temperature of 1100 K, Fig. 1 shows the composition oscillating from layer to layer, with the deviations from the bulk composition decaying rapidly away from the surface. At lower temperature, the composition variations extend deeper into the slab. At 700 K, the oscillations appear to decay only very slowly away from the surface, indicating that this temperature is close to or below the bulk ordering temperature T_c . Our best estimate of T_c from bulk simulations is around 800 K, in satisfactory agreement with the experimental value of about 680 K.

These Monte Carlo simulations clearly illustrate the connection between oscillatory segregation at high temperatures, and bulk ordering at low temperature. For CuAu(100), the former grows continuously into the latter as the temperature is reduced. In analogy with surface premelting, which similarly diverges in depth as the bulk transition temperature is approached, this oscillatory segregation could as well be called "surface preordering."

General treatments of surface segregation (as opposed to numerical calculations for specific systems and temperatures) have almost universally assumed that only the surface layer deviates appreciably from the bulk composition.⁹ To go beyond such a restrictive assumption, we begin with the usual Ising-like model for the alloy energy,

$$U = J \sum_{m \neq n} (1 - \delta_{\sigma_m \sigma_n}) .$$
⁽²⁾

Here U is the enthalpy of mixing, σ_m identifies the species of atom m, and the sum is restricted to nearestneighbor pairs. This formula represents a fixed pair interaction J between neighboring unlike atoms, and no interaction between like atoms. We are primarily concerned with the case J < 0, since this yields bulk ordering and oscillatory surface segregation. The size difference between atoms and associated strain effects is neglected, since the point here is only to capture the qualitative behavior.

The properties of the alloy can then be calculated within a mean-field model, where each layer parallel to the surface is characterized by a mean composition x_n , signifying $\operatorname{Cu}_{1-x}\operatorname{Au}_x$ in layer *n*. The entropy per atom in layer *n* is then $S = -k[x_n \ln x_n + (1-x_n)\ln(1-x_n)]$, where *k* is the Boltzmann constant. The enthalpy is calculated as a function of the layer compositions x_n simply by counting the average number of unlike bonds to neighbors in each layer. The chemical potentials are determined by equilibrium with the bulk.

For convenience, instead of x_n we work with the variable $w_n \equiv 1 - x_n / x$, where an unsubscripted x denotes the bulk composition. Thus w = 0 for the random alloy.

By minimizing the free energy with respect to the composition of layer n, we obtain a recurrence relation for (100) layers,

Equation (3) is valid for all layers which are not directly perturbed by the surface, typically all but the first layer.⁹ (An exception, CuNi, is discussed below.) In combination with the surface boundary condition (which involves the difference of surface energies for the two types of atoms), Eq. (3) yields the complete behavior of the (100) surface within the mean-field approximation to the model (2). The transition temperature for bulk ordering is obtained by taking $w_n \propto (-1)^n$ and vanishingly small, giving $kT_c = -16Jx (1-x)$.

At temperatures above T_c , the deviations from randomness induced by the surface segregation must decay with distance into the bulk. This decay is exponential when w is small, i.e., everywhere except very near the surface. Solving the recurrence relation (3) for $w \ll 1$ yields

$$w_n \propto (-1)^n e^{-n/\nu} , \qquad (4)$$

where

$$v_{(100)} = \operatorname{sech}^{-1} \left[\frac{1}{2} + \frac{1}{2} \frac{T}{T_c} \right] .$$
 (5)

Note that as $T \rightarrow T_c$, $\nu \rightarrow \infty$, i.e., the decay length of the surface oscillations diverges at the bulk ordering temperature. Below this temperature, the segregation may still

be enhanced near the surface, but it will decay only to a finite bulk value.

The interpretation of experimental data for NiPt(100) is problematic, because the surface layer reconstructs.² But data are also available for the (111) and (110). For brevity we consider only (111) layers; an atom in a (110) layer has neighbors two layers away, making that case more complicated. Rederiving Eq. (3) for (111) layers gives

$$w_{n-1} + w_{n+1} + \left[2w_n - \frac{kT}{12Jx} \ln \left[1 + \frac{w_n}{(1-x)(1-w_n)} \right] \right] = 0.$$
 (6)

Equation (6) yields no bulk order at any finite temperature, since (111) ordering does not affect the number of unlike neighbors in the bulk. Of course, below T_c , a mean-field model with (111) layers is inappropriate, since the system will actually order in the [100] direction.

Any surface-induced nonrandomness again decays exponentially following Eq. (4), but with

$$v_{(111)} = \operatorname{sech}^{-1} \left[1 + \frac{2T}{3T_c} \right].$$
 (7)

Thus even near T_c , the segregation at the (111) surface decays asymptotically by a factor of 3 with each layer. This corresponds to an exponential decay length v of about one layer, so segregation is confined to a very few layers at this surface.

The prediction of this simple model was confirmed by full Monte Carlo calculations with the empirical potential. In the temperature range of Fig. 1, CuAu(111) showed only a small enhancement of the Cu concentration in the second layer, with no significant oscillations in deeper layers.

The actual experiments of Ref. 2 involved annealing PtNi samples at 1200 K, about $1.3T_c$ for the 50-50 alloy. At this temperature, the (111) decay length v is only 0.8 layers. In contrast, for the (100) orientation, the decay length would be about two layers. Thus dramatic differences in the depth of the oscillations are predicted for different surface orientations. Unfortunately, the analysis of Ref. 2 allows only three layers to be treated as different from the bulk composition. Application of the atom-probe method¹ to these surfaces would thus be of considerable interest, since it has no such restriction.

The results here for CuAu bear directly on the PtNi experiments,² because of the great similarity of the two alloys, and in particular of their phase diagrams. The other system in which oscillatory segregation has been observed is PtRh.¹ Despite one early suggestion,¹⁰ bulk ordering in PtRh has never been confirmed. The question thus remains, whether the present results can explain the PtRh data even qualitatively.

One possible explanation lies in the dependence of the effect on orientation. The PtNi data, as discussed above, show a significant oscillation in the first three layers or so for a (111) surface, where the asymptotic decay length v was here estimated to be roughly 0.8 layers. The PtRh data show even shallower oscillations than the PtNi(111),

and so presumably correspond to a decay length at least as short. However, the PtRh data are for a (100) surface. According to Eq. (5), to have a decay length of less than 0.8 layers at a (100) surface, the temperature must be quite high relative to the bulk ordering temperature, $T \ge 2.7T_c$.

Since equilibration of PtRh was performed at $700-800^{\circ}$ C (~1000 K), the inferred relationship $T \ge 2.7T_c$ implies a critical temperature $T_c < 400$ K for the composition used. This number should not be taken too seriously; but if it is anywhere close to correct, such ordering could never be observed, because there is not sufficient mobility at such a low temperature for equilibration. Thus it is consistent and reasonable to speculate that PtRh has a very weak tendency to order, which is sufficient to induce oscillatory segregation at a (100) surface, but which would presumably be undetectable at a (111) surface (or in the bulk). This speculation is further supported by the unremarked presence of small but statistically significant oscillations in deeper layers of PtRh.¹

A third system, CuNi, has been reported^{5,11} to exhibit oscillatory segregation, but is really not comparable. In that case, the composition apparently reverses only once, between the first and second layers. Foiles⁵ showed that this reversal is driven by a layer-specific effect, analogous to the Si-Ge surface.⁴ Past the second layer, the segregation is monotonic, and corresponds to the behavior discussed below for alloys having a miscibility gap. Analogous behavior in alkali-metal alloys has also been predicted by Barnett *et al.*¹²

Finally, it is interesting to compare the case of an ordering alloy, J < 0, to that of a segregating alloy, J > 0. Equations (3) and (6) relating successive layers are still valid, leading to an asymptotic behavior $w_n \propto e^{-n/\nu}$. This is similar to Eq. (4) except that the composition no longer oscillates, it decays monotonically. Such behavior has indeed been observed for Pt-Au, a segregating alloy, by Tsong *et al.*¹³ Calculations for CuNi show similar behavior beyond the second layer,⁵ where the recurrence relations (3) and (6) apply.

As T approaches T_c , the temperature for the onset of segregation at the given composition, $v \to \infty$ as before. However, unlike the case of oscillatory segregation, here the depth of the effect diverges at T_c regardless of orientation, although the value of v for $T > T_c$ does depend on orientation.

Thus, in both oscillatory and monotonic surface segregation, the bulk phase diagram of the alloy is seen to play a crucial role. To test these ideas, it would be particularly interesting to study the segregation of both ordering and segregating alloys near T_c , where the effects are predicted to be most dramatic and most strongly temperature dependent.

In conclusion, Monte Carlo simulations of a CuAu surface predict oscillatory segregation, similar to that which has been seen experimentally for PtNi and PtRh. The driving mechanism for this oscillation has two components. First, the surface energy difference drives Au to the surface layer. Then, the tendency to favor bonds between unlike atoms in this system drives Cu to the second layer where it has extra Au neighbors, then Au to the third layer where it has extra Cu neighbors, etc.

Above the bulk ordering temperature T_c , these oscillations decay exponentially into the bulk. The decay length diverges at T_c if the surface orientation corresponds to the bulk ordering direction. Analogous behavior occurs in monotonic segregation for alloys with a bulk miscibility gap. The connection proposed between surface segregation and the bulk phase diagram should provide a guide in selecting alloys, orientations, and temperatures for future examination in studying this phenomenon.

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reducing the number of parameters from nine to four per element. In the present application, the cutoff distances R and S are unimportant, as long as they fall between the first- and second-neighbor distances.

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