VOLUME 74, NUMBER 3 PHYSICAL REVIEW LETTERS 16 JANUARY 1995

Surface-Confined Alloy Formation in Immiscible Systems

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(Received 2 September 1994)

Elements which are immiscible in the bulk have been found to form stable two-dimensional mixtures at the free surface. Here we show that such surface-confined mixing is expected quite generally in systems which are dominated by the atomic size mismatch. Mismatch renders the elements immiscible in the bulk, and confines the minority species to the surface, while inhibiting it from segregating within the surface layer. However, a large interface energy will cause clustering within the surface layer. This strain-dominated scenario is consistent with a variety of experimental observations.

PACS numbers: 68.55.–a

The formation of alloys is one of the classic problems of materials physics. It is thus remarkable that, in the last year, four Letters [1–4] independently reported a novel kind of two-dimensional alloy. These studies examined Na and K deposited on Al(111) and (001), Au on Ni(110), Ag on Pt(111), and Sb on Ag(111), respectively. In each case it was found that a pair of elements, which are immiscible in the bulk, would readily form a mixture confined to a single atomic layer at the surface. Related behavior has been seen in other systems as well [5–7]. The possibility of forming novel alloys, which exist only at surfaces, has important implications for surface chemical processes such as heterogeneous catalysis.

In three cases [1,2,4], careful theoretical calculations were performed to determine the energetics in those particular systems. Such an approach is essential for a detailed understanding of specific cases. However, recognizing that the phenomenon occurs in many systems, it seems important to also seek a more general explanation, which would complement the analyses of specific cases.

Here we show that surface-confined mixing arises *generically* in systems dominated by atomic size mismatch. This explains why the phenomenon is surprisingly common, and also why it has been observed particularly in systems with substantial mismatch in atomic sizes. We also show that a positive interface energy, in combination with the size mismatch, leads to formation of finite-size clusters within the surface layer, as are seen experimentally [2,3,5]. These conclusions are supported both by an analysis of the energetics, and by Monte Carlo simulations, which reproduce the general behavior seen experimentally.

As discussed by Röder *et al.* [3], the simplest framework for understanding binary systems is in terms of surface and interface energies. This macroscopic approach ignores details of the atomic structure, yet it is highly successful in accounting for growth morphology and intermixing in many systems. When a material A is deposited on a substrate B, the system may be characterized by the respective surface energies γ_A and γ_B, and by the interface energy γ_{AB}. If $\gamma_{AB} \leq 0$, the two materials can lower their energy by intermixing. Otherwise material A will segregate; in that case it will or will not wet B, depending on whether or not $\gamma_A + \gamma_{AB} < \gamma_B$.

This viewpoint, however, cannot fully explain the experimental observation of surface-confined mixing. If $\gamma_{AB} < 0$, then A will dissolve into the substrate; otherwise, A will segregate, either into a continuous wetting layer or into large islands or inclusions. It is conceivable that a very small γ_A could confine species A to the surface even for $\gamma_{AB} < 0$, giving a surface-confined alloy. However, the two elements would then be continuously soluble in the bulk; this was not the case for any of the systems studied [1–4].

One limitation of this classic perspective is that it considers only energy, and neglects kinetics. However, arguments based on energetics, where applicable, are far more general than those based on kinetics. Moreover, the simple picture above works well for many systems, indicating that the kinetics of surface mixing are not excessively restrictive. We therefore look for a resolution in the description of the energetics, rather than in an appeal to kinetics.

The principal feature missing in the above picture of the energetics is strain. When the atoms have different sizes, this may lead to phenomena which cannot be understood in terms of surface and interface energies, such as coherent Stranski-Krastonow growth [8,9]. It is already known that atomic size mismatch may lead to surface segregation. Strain is also known to drive intermixing in the bulk [10] and at the surface [6]. What is remarkable here is that the same effect, the atomic size mismatch, suppresses intermixing in the bulk while favoring intermixing at the surface.

To better understand the role of atomic size mismatch, we calculate in detail the behavior of a highly simplified model which contains *only* strain energy. Specifically, we assume a pair-wise interaction between neighboring atoms, using a form like the two-body part of the Keating model [11],

$$E = \alpha \sum_{ij} (r_{ij}^2 - b_i b_j)^2. \tag{1}$$

Here r_{ij} is the distance between atoms i and j, and the sum is restricted to nearest-neighbor pairs. The preferred bondlength of atom i is b_i, and the bond stiffness is given by α. For small displacements, this gives a Hook's law interaction between neighboring atoms.

For concreteness, we discuss Au deposited on Ni(001). However, here and throughout this Letter, references to "Au" and "Ni" should *not* be taken literally. The names of real elements are used merely as a convenience. Since the model contains *only* strain energy, it does not accurately describe any specific real material; it is intended only to isolate the effect of atomic size mismatch.

The bondlengths are $b_{\mathrm{Ni}} = 2.49$ and $b_{\mathrm{Au}} = 2.88$ Å. An appropriate choice of α reproduces the three elastic constants of Ni to better than 10%. The bulk modulus of Au is similarly well described, although its anomalously soft shear constant is not.

Energies of relevant atomic configurations are calculated using a $c(8 \times 8)$ supercell (32 atoms per layer), with the free surface described by a 16-layer slab. The geometry is relaxed until all forces are less than 5×10^{-4} ev Å^{-1} (10^{-5} a.u.). The results are summarized in Table I. All energies are as given by Eq. (1). This is equivalent to using bulk Ni and bulk Au as the thermodynamic references.

Consider first a single Au atom. In the Ni bulk it has a rather high elastic energy, 0.45 eV. This immediately implies that the two metals are immiscible: The fractional solubility of Au in Ni within this model would be $e^{-0.45\mathrm{eV}/kT}$, less than 1% at temperatures up to $T = 800\,^\circ\mathrm{C}$. (However, two elements which we call immiscible, because they do not form continuous solutions, may nevertheless be able to form bulk compounds at special stochiometries which minimize the strain energy.)

In contrast, the elastic energy at the surface is much lower, 0.09 eV. This occurs because strain is partially relieved by the presence of a surface. As a result, the Au strongly prefers to be at the surface, even in the absence of any surface-energy effects. Similar behavior was discussed by Oppo *et al.,* [4] for Sb on Ag(111).

TABLE I. Calculated energies for Au on Ni (001), from Eq. (1), in electron volts (eV) per Au atom. (ML = monolayer. Model contains only strain, and so does not correspond to real Au and Ni.)

	Relaxed	Unrelaxed
Au atom in:		
Surface	0.092	0.382
Layer 2	0.429	0.573
Bulk	0.449	0.573
Au atoms in surface layer:		
Isolated	0.092	0.382
Nieghboring pair	0.132	0.431
2nd neighboring pair	0.089	0.382
$\frac{1}{2}$ ML $c(2 \times 2)$:	0.158	0.382
1 ML	0.384	0.575

Given a fraction of a monolayer of Au on the surface, our calculations show that the Au prefers to remain dispersed as an alloy. From Table I, two Au atoms in the surface layer repel each other, with an energy of 0.08 eV higher when they are neighbors than when they are far apart. This repulsion may be viewed as arising from overlap of the strain fields surrounding the two atoms. There is, however, a slight *attraction* in the second-neighbor position, which favors $c(2 \times 2)$ ordering. Such ordering is in fact seen when Au is deposited on Cu(001) [7].

The table also gives energies for 50% and 100% Au in the surface layer. Because of the strain-mediated repulsion, the greater the Au concentration, the greater the energy *per Au atom.* Thus the Au will remain dispersed for all coverages below 1 monolayer.

These effects may be augmented or opposed by other contributions to the energy: a positive or negative interface energy; a difference in surface energy for the two atoms; or the possibility of more complex structures, such as surface reconstructions. For material A deposited on B, if A has lower surface energy ($\gamma_A < \gamma_B$), then the tendency for A to be confined to the surface layer would be enhanced; $\gamma_A > \gamma_B$ would oppose this tendency. A negative interface energy $\gamma_{AB} < 0$ would enhance the tendency of A to remain dispersed in the surface. However, if γ_{AB} is too negative, it could render the materials miscible in the bulk, despite the misfit.

Perhaps the most interesting situation occurs when there is a positive interface energy, $\gamma_{AB} > 0$. Then the interface energy drives lateral segregation of A within the surface layer, to minimize the interface area within the first layer. (The area of interface between the first and second layers is independent of the arrangement of A atoms within the surface layer.) However, this γ_{AB} driven segregation is opposed by the effect of misfit. There is significant elastic relaxation near the edges of the strained A clusters, so the strain energy is lower for small clusters than for large ones, and lowest for dispersed A atoms.

This competition between interface energy and elastic relaxation has been analyzed in detail, in a rather different context, by Vanderbilt and Wickham and Alerhand *et al.* [9,12]. The energy is minimized when element A segregates into patches with spacing

$$L \propto e^{\lambda M/\sigma^2} / \sin(\theta \pi/2)\,. \tag{2}$$

Here θ is the coverage (in monolayers), σ is the two-dimensional stress of a monolayer of element A, M is an elastic constant, and λ is the energy per unit length of the patch edge (in effect γ_{AB} times the layer thickness). This provides a natural explanation for the observation of Röder *et al.* [3], that deposition of Ag on Pt(111) led to 10–13 Å patches within the surface layer, rather than to atomic dispersal. Similar behavior was seen by Chambliss and co-workers [5] for Fe deposited on Cu(001), and two-atom clusters were seen by Nielsen *et al.* [2] for Au on Ni(110), where the surface layer is comprised of distinct rows of atoms.

Before discussing Monte Carlo simulations which illustrate this behavior, there are several technical points which should be addressed. We have not considered adatoms or small islands, but only atoms substituted into the surface or bulk, or forming continuous adlayers. Adatoms or atoms at steps have reduced coordination, i.e., "dangling bonds," and so are energetically rather unfavorable [13]. Thus deposited atoms, if sufficiently mobile, generally will form large islands, where the large terrace-edge ratio renders the step energy relatively unimportant, or else they will substitute into the surface, with the ejected atoms forming large islands. In either case, the energetics is adequately modeled by a continuous layer with the appropriate composition. We do not consider cases where the misfit is so great as to preclude mixing, or to allow the formation of an incommensurate monolayer.

In principle, if a macroscopic amount of material is deposited, then all of the geometries in Table I are metastable. The true thermodynamic ground state of the system involves macroscopic segregation of the Au into a relaxed island. However, this ground state is relatively inaccessible kinetically. Only when the Au becomes thick enough to form dislocations, and so relax the strain in the film, will macroscopic segregation become favorable. But the energy of a thick Au layer pseudomorphic on Ni is calculated to be 0.4 eV/atom, much higher than the surface alloy. Thus as long as there is well under a monolayer of Au in all, there is a large barrier to coalescing into a multilayer island, a necessary precursor of strain relaxation.

The known examples of surface-confined alloying all involve deposition of a larger atom onto a small one: alkali metals on Al, Au on Ni, Ag on Pt, and Sb on Ag. To test for an inherent asymmetry, the above calculations were repeated for Ni on Au. The results were very similar to those for Au on Ni. If an asymmetry is observed experimentally, it may originate in factors other than the strain, e.g., from a correlation of surface energy or surfaces stress with atomic size.

Finally, while the model (1) lets us clearly identify the effects of strain alone, it can be very difficult to isolate strain effects in less simplified calculations. One can more readily identify *relaxation* effects, as Nielsen *et al.* did [2], by comparing relaxed and unrelaxed geometries. It is thus instructive to note that the strain effects discussed here occur *even in the unrelaxed geometries* in Table I.

To test whether the effects discussed above are sufficient to explain the observed behavior, we have performed Monte Carlo simulations of the distribution of Au atoms on Ni(001). These simulations include random motions of the atoms, but also allow random exchanges of Au and Ni atoms, to permit efficient compositional equilibration [14,15].

For total coverages of $\frac{1}{2}$ and $\frac{1}{4}$ monolayer, we calculate the equilibrium distribution of Au at 600 K. Using the same $c(8 \times 8)$ cell as above, the configuration is first equilibrated for 8000 steps per atom, and then averaged over 5000 steps per atom. The resulting composition profile for $\frac{1}{2}$ monolayer is shown in Fig. 1. While the surface layer remains about 40% Au, the Au fraction decreases exponentially with depth [16]. Even the second layer has under 10% Au, with much less in subsequent layers. For an initial coverage of $\frac{1}{4}$ monolayer, there is less than 1% Au in the second layer. (This sensitive dependence upon coverage presumably arises because the Au chemical potential is a highly nonlinear function of coverage.) Thus even at this elevated temperature, the Au is confined rather effectively to the surface [15], especially at low coverage.

In order to address the distribution of Au *within* the surface layer, we perform a second set of simulations for $\frac{1}{4}$ monolayer of Au, using a larger $c(16 \times 16)$ cell, i.e., 128 atoms per layer. We introduce a nonzero interface energy γ_{AB} by adding an energy Δ_{AB} for each bond between an A atom and a B atom. The system is heated to 600 K, and then quenched at a rate of 30 steps per atom per degree Kelvin. For an unconstrained simulation like that described above, the final distribution after quenching has almost no Au below the first layer. Therefore, for computational efficiency, and to simplify interpretation, we chose not to allow Au atoms to move to subsurface sites in subsequent simulations. Also, atoms below the seventh layer were fixed at their ideal positions.

The resulting surface structures after quenching are shown in Fig. 2. Values of Δ_{AB} are indicated, and a random distribution is shown for comparison. For $\Delta_{AB} = 0$, the distribution is actually more uniform than the random distribution, because of the mutual repulsion. In fact, for $\Delta_{AB} = 0$, few Au atoms have a Au neighbor, while for the random distribution they each have on average one Au neighbor.

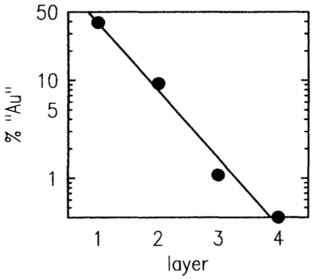
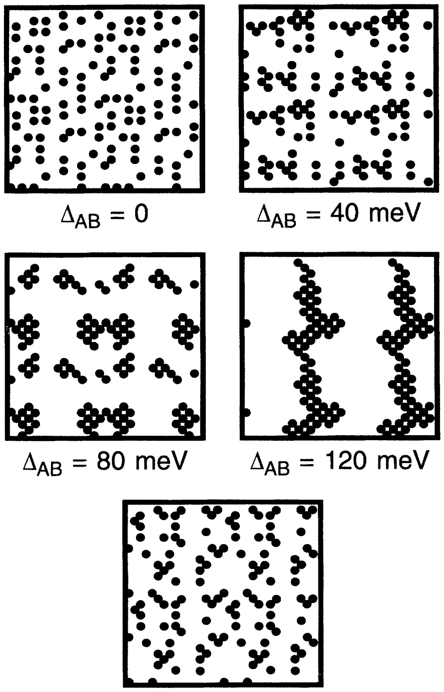


FIG. 1. Equilibrium percentage of minority atom (called Au here) in each layer, from Monte Carlo simulation at 600 K as described in text. Initial coverage is $\frac{1}{2}$ monolayer. Layer 1 is surface. The straight line is least-squares fit.



$\Delta_{AB} = 0$ $\Delta_{AB} = 40$ meV

$\Delta_{AB} = 80$ meV $\Delta_{AB} = 120$ meV

random

FIG. 2. Distribution of Au atoms within surface layer, after Monte Carlo quenching as described in text. Results are shown for four indicated values of Δ_{AB}, the energy cost per A-B bond. A random distribution is shown for comparison. Each image corresponds to four unit cells, periodically repeated for visual clarity. The dot size is chosen to just touch for neighboring atoms.

For increasing Δ_{AB}, there is an increasing tendency toward clustering. The quench rate is apparently too fast to obtain clusters of uniform size, and the cell size constrains the possible cluster spacings. Nevertheless, the trend is clear. For $\Delta_{AB} \gtrsim 120$ meV, there is only one large cluster per unit cell, i.e., the cell size is too small to describe the natural cluster spacing. In contrast, for $\Delta_{AB} = 40$ meV, the preferred cluster size appears to be only a few atoms, and perhaps 10 atoms or so for $\Delta_{AB} = 80$ meV. Despite the quenched-in disorder, these simulations clearly corroborate the general tendency to clustering described in Eq. (2).

While we have used a particular model system to illustrate several points, the points themselves are independent of the specific system. It is *generally* true that a misfitting atom will have reduced strain energy at the surface, relative to the bulk. It is also *generally* true that strain will cause two misfitting substitutional atoms in the surface to repel. Thus, *to the extent that the energetics are dominated simply by strain effects,* one expects the two elements to be immiscible in the bulk, but nevertheless to form an alloy confined to the surface. Without detailed calculations, such as those in Refs. [1,2,4], it is not possible to predict with confidence how any given system will behave. But the generic strain-dominated behavior, modified by γ_{AB} driven clustering, is exactly what is seen in many systems.

Helpful discussions with A. Zangwill and R. M. Tromp are gratefully acknowledged. This work was supported in part by ONR Contract No. N00014-92-00085.

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[15] In true equilibrium, for a semi-infinite substrate of pure Ni, the Au would all dissolve into the bulk, even though each layer can hold only a negligible amount. However, on laboratory time scales mixing can only take place between a few layers near the surface, so our finite-slab simulation is quite appropriate.

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