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Enhanced solubility on surfaces: Molecular-dynamics simulations of an Ag overlayer on Cu(100)

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Using molecular-dynamics simulations, we calculate the energetics of Ag deposited on Cu(100) surface and show that the driving force for substitutional surface alloying diminishes with increasing Ag coverage at 300 K. We further demonstrate that even at the Ag saturation coverage of close to one monolayer, the apparent positive enthalpy of mixing in surface layers is reduced relative to its value in the bulk and decreases with increasing temperature. As a result, intermixing between the reconstructed Ag overlayer and the underlying Cu surface layer can be observed at moderately elevated temperatures, forming a surface alloy well beyond equilibrium solid solubility limits.

During the past few years, a number of experiments of initial metal-on-metal deposition have shown that surface alloying occurs in metal systems which are characterized by a positive heat of mixing (ΔH) and known to exhibit negligible solid solubility in the bulk, e.g., Refs. 1–7. Surface alloying of Ag deposited on single-crystal Cu(100) into the first layer of Cu near room temperature ($\mathrm{RT}=300\,\mathrm{K}$) is a typical example of this behavior, despite the fact that bulk Ag has a lower surface energy than Cu.[6,7] At low Ag coverages <0.13 monolayer (ML), the incoming individual Ag atoms replace the Cu atoms in the first substrate layer, forming a substitutional alloy confined to the two-dimensional (2D) surface. This phenomenon was found energetically favorable based on energy calculations within the effective-medium theory in similar systems (e.g., Au-Ni),[1,7] as the highly undercoordinated surface atoms strive to increase their effective coordination or electron density. However, with increasing Ag deposited, phase separation was observed, presumably driven by the increasing tendency for Ag to attach to large patches. When the Ag coverage reached saturation (0.9 ML), the surface was observed to become completely dealloyed with a hexagonal Ag(111) overayer on top of a nonalloyed Cu(100) substrate.[6,7] As such, surface alloying is a 2D phenomenon only at low, subsaturation coverages.

In this paper, we perform a molecular dynamics (MD) simulation to investigate the alloying behavior and the evolution of the alloying driving force for Ag deposited on Cu(100). We show that while a driving force for intermixing between Ag and Cu exists for low Ag coverage at RT, the sign of the energy difference between the unalloyed and alloyed states is reversed as the coverage approaches saturation, eventually rendering intermixing energetically impossible at RT. The focus of this work, however, is to demonstrate that even at such high coverages, intermixing between the Ag overlayer and the Cu layer underneath can be observed well beyond the equilibrium bulk solubility limits at moderately elevated temperatures. The energetics of the alloyed and unalloyed surface configurations, including both the enthalpic and entropic contributions, are monitored using MD simulations and compared with the bulk cases over a range of temperatures. The results indicate that, compared with the positive ΔH in the bulk arising from the large atomic size difference between the two elements, the effective ΔH is apparently reduced in the surface layers, especially at elevated temperatures. The surface effects on the alloy energetics and their temperature dependence are proposed to be responsible for the enhanced solubility observed.

MD simulations have been performed in the constant pressure, constant temperature (*N-P-T*) ensemble. The MD cell consisted of Ag atoms with different fractions of a Ag monolayer $[1\text{-ML Ag}\,(111)=1.38\times10^{15}\,\text{atoms/cm}^2]$ deposited over 10 (100) layers of Cu atoms with 128 atoms/layer using a $c(16\times16)$ supercell. Ag atoms were deposited using a rigid 2D adlayer of a random structure uniformly placed above the surface just within the force range of its nearest surface atoms. Periodic boundary conditions were applied in the directions parallel to the surface. Classical equations of motion for all atoms were solved numerically during each time step using standard techniques, as the system was relaxed and annealed. After reaching equilibration at the desired temperature, statistics were accumulated over an additional 50–200 ps. The mean-square vibrational amplitudes and the thermodynamic properties were then calculated.

The interaction potentials used for Ag-Cu are based on the embedded atom method (EAM).[8] The EAM potentials have been successfully used in predicting several surface properties such as relaxation, reconstruction, and the dispersion of the surface phonons for Ag, Cu, and Ni.[8–11] For Ag-Cu, an EAM potential was employed in a previous study that correctly reproduced the experimental ΔH of solid solutions and equilibrium solid solubilities (with solute content <10 at. %).[12] For the equiatomic composition, our simulation gives a bulk ΔH of 6.8 kJ/mol at RT, which agrees well with the value of $7.0\pm0.5\,\mathrm{kJ/mol}$ obtained in our recent calorimetric measurements using cosputtered thick $\mathrm{Ag}_{50}\mathrm{Cu}_{50}$ foils. This EAM potential is therefore used rather than an empirical *n*-body potential developed more recently for Ag-Cu by Mazzone *et al.*,[13] which predicted a $\Delta H=+13.2\,\mathrm{kJ/mol}$ for the random solid solution at the equiatomic composition.

The Gibbs free energy of the system was computed by adding together the three contributions due to the bonding energy, atomic vibrations, and the configurational entropy.[12,14,15] The cohesive (bonding) energy, which is used to approximate the enthalpy of the system at ambient pres-

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sure, is calculated within the EAM framework.[8] The vibrational contribution to the free energy is determined through MD using the local harmonic (LH) model.[12,14,15] The configurational entropy contribution to the free energy is written based on the formula for ideal entropy of mixing (Bragg-Williams approximation), with modifications made to approximate the real alloy with clustering tendencies,

$$E_{\mathrm{conf}} = -Nk_BT(x_a' \ln x_a' + x_b' \ln x_b'), \tag{1}$$

where N is the total number of atoms in the system, and x_a' is the probability that an atomic site is occupied by the solvent atom a, and correspondingly, x_b' is the probability that the same site is occupied by the solute atom b. x_a' and x_b' are estimated from MD simulations and different from the nominal compositions x_a and x_b (Ref. 16) to take into account the effect of solute clustering.

As shown below and in experiments,[6,7] only the atoms in the top two atomic layers are observed to involve in alloying. As Ag has a lower surface energy than Cu, segregation and confinement of Ag to surface layers is expected[7,17] and predicted by first-principles calculations.[18] Our simulations show that for atoms beyond the third layer, little change in energy is observed between the unalloyed (Ag on Cu) and alloyed (the Ag overlayer intermixes with the first Cu layer) states. Calculations of the changes in system energy were therefore made by summing up the interactions of the atoms within the first three atomic layers with all the atoms in the system.

Our MD simulation of 0.07-ML Ag atoms deposited and randomly distributed on Cu(100) at 300 K, before and after alloying, indeed indicated the presence of a driving force for intermixing. The enthalpy difference between the as-deposited unalloyed state and the alloyed state is 12.3 kJ/mol. Indeed, in experiments at 440 K (needed to overcome the activation barrier[6,7]), alloying of Ag into the first Cu layer has been observed. However, when the Ag coverage is increased to 0.5 ML and then further to 0.9 ML at the same temperature, after 100 ps of relaxation and reconstruction the Ag atoms evolve into a pure Ag overlayer with a nearly hexagonal configuration, Fig. 1. This observation is consistent with previous experimental[6,19,20] and theoretical[21,22] findings that the Ag overlayer deposited on Cu(100) has a reconstructed $c(2\times10)$ structure with every tenth atom at a hollow site. No intermixing is observable between Ag and the Cu layer underneath, even after prolonging the simulation time to 1 ns, again in agreement with the experimental observations.[6,7] Comparing this unalloyed system (Fig. 1) with an alloyed state (the top two layers arranged to intermix into a nearly equiatomic alloy), the latter now is higher in enthalpy by 4.2 kJ/mol. Apparently, at such a high coverage, the apparent ΔH is sufficiently positive to preclude any observable solubility near RT.

However, it is noticed that the enthalpy difference is now about 40% lower than the positive ΔH in the bulk equiatomic Ag-Cu alloy. This may be attributed to the fact that the strain induced by alloying size-mismatched Ag and Cu is more easily accommodated in the low-dimensional surface layer with no atomic coordination above. In fact, our simulations do not lattice match with the substrate and have predicted that adding a small percentage of Cu atoms into the reconstructed hexagonal Ag overlayer actually lowers its energy, consistent with Ref. 18 which showed that the $c(10\times2)$ hexagonal phase is the most stable with about 10 at.% Cu solute. The apparent overall ΔH (still positive) is mainly due to the energy cost from substituting Ag into the Cu layer underneath. The reduced energy penalty for alloying points to the possibility of enhanced mutual solubility, which indeed becomes observable at elevated temperatures. As seen in Fig. 2, MD simulation at 800 K after 200 ps shows pronounced intermixing between the surface layers well above the equilibrium bulk solubility limits [3 at. % Cu in Ag and 1 at. % Ag in Cu (Ref. 23)]. There appears to be a tendency for the substitutional atoms in both layers to cluster. Prolonged runs showed no further changes, suggesting a saturation of solubility at about 14 at. % Cu in Ag, and 11 at. % Ag in Cu at 800 K.

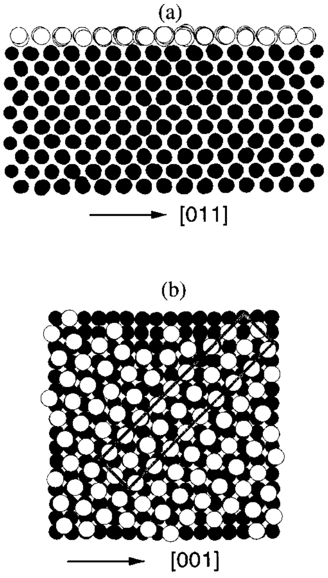

FIG. 1. 0.9-ML Ag (open circles) on Cu (100) at 300 K (200 ps), (a) side view and (b) top view, showing the hexagonal Ag overlayer with a $c(2\times10)$ structure.

The energy difference between the alloyed configuration (Fig. 2) and the unalloyed state (Fig. 1) have been monitored as a function of temperature to see how and when a driving force for alloying appears. At temperatures <800 K, the alloyed structure was obtained by annealing the system after quenching the alloy from 800 K. The enthalpies of the two states are shown in Fig. 3(a). The enthalpy difference, while always consistent with an apparent positive ΔH in the system, is found to decrease with increasing temperature, presumably due to the increasingly easier accommodation of strains associated with alloying in the surface layers (additional simulations indicate that the temperature dependence of the ΔH is very weak in the bulk, only a few percent change between 300 and 800 K). This additional reduction of the apparent ΔH with temperature further lowers the barrier to Ag/Cu reaction. To understand the driving force for alloying, at finite temperatures one should assess the changes in Gibbs free energy, incorporating the entropic contributions. The vibrational entropy contribution was computed in the MD simulation based on the LH model. It was observed that the alloyed state has a lower vibrational entropy than the unalloyed state, probably due to the stiffening of bonds.

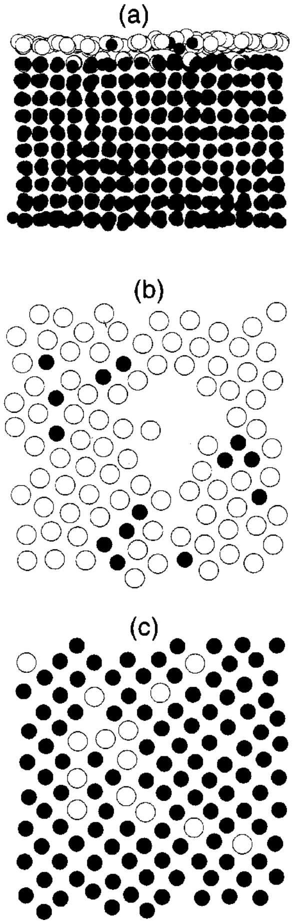

FIG. 2. 0.9-ML Ag (open circles) on Cu (100) at 800 K (200 ps), (a) side view, (b) top view of the top surface layer, and (c) top view of the second layer, showing the intermixing of the Ag adlayer and the top layer of Cu (100).

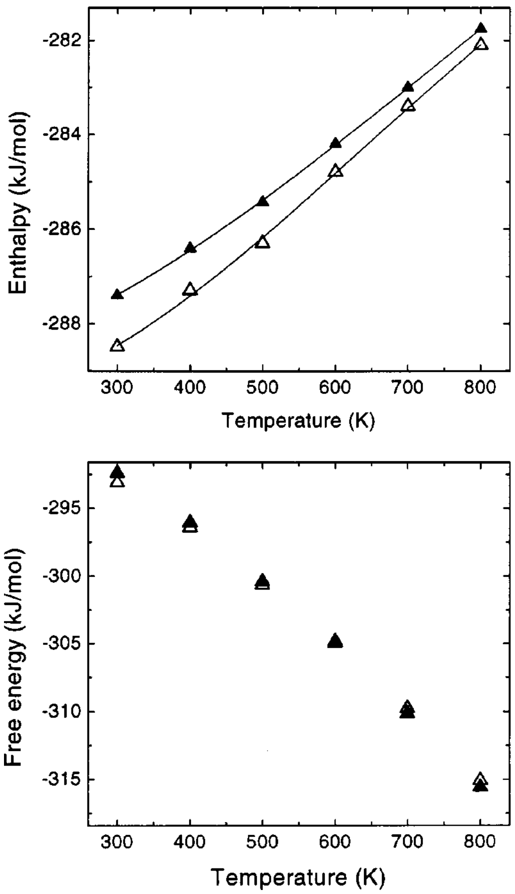

FIG. 3. The enthalpy (a), and free energy (b) for the alloyed (full triangles, configuration in Fig. 2) and unalloyed (open triangles, configuration in Fig. 1) 0.9-ML Ag on Cu (100), as a function of temperature.

Since this vibrational contribution turns out to be only 18 (at 300 K) to 35% (800 K) of the configurational part calculated using Eq. (1), our LH estimate neglecting anharmonic contributions suffices. Adding the entropic contribution, which drives intermixing, to Fig. 3(a) yields the free energies of the two states shown in Fig. 3(b). It is seen that while the extended solubility (Fig. 2) is energetically unfavored at RT, a driving force does become available at about 600 K. Apparently, with increasing temperature the increasing entropic contribution and the decreasing apparent ΔH are responsible for the pronounced extension of solubility beyond equilibrium bulk values observed in Fig. 2. Note also that the alloy formed (Fig. 2) shows signs of clustering to some extent. In a system with positive ΔH such an alloy has a reduced enthalpy with respect to a random solution of the same composition.

It is well recognized that bimetallic surfaces, with undercoordinated atoms, reduced dimensionality, and sometimes lattice mismatch with the substrate, can have phase diagrams and a wealth of phenomena quite different from those of the bulk.[18] For example, it has been shown that when codeposited into a monolayer, Ag and Cu appear to have *negative* surface mixing energy and are miscible at ambient temperatures on top of Ru(0001) (Ref. 5) due to the effects of strain relief in matching with the substrate, and on top of Cu(100) (Ref. 18) both in pseudomorphic and nonpseudomorphic cases. The latter case has also been verified in our MD simulations. Our case of the reaction between a reconstructed Ag overlayer and the first ML of Cu(100) is another manifestation of the favorable alloy energetics on surface. In bulk Ag-Cu, the large size mismatch between Ag and Cu results in a positive ΔH sufficiently high to restricts the solubility to no more than a couple of at. % at $<$ 800 K. On surface, in contrast, the constraint is partly removed. In fact, as discussed by Tersoff for system dominated by a large size mismatch,[24] which for the present Ag-Cu system is 13%, strain effects can also favor alloying on surface even though they suppress intermixing in the bulk. Large misfitting atoms will have reduced energy at the surface so as to be confined in the surface layers instead of penetrating into the bulk. Indeed no Ag atoms moved beneath the first Cu layer (Fig. 2). Furthermore, these atoms will repel each other to further increase the possibility of strain relaxation, favoring intermixing. This tendency of dispersion is in competition with the positive interface energy between the two species. The resulting balance can be clustering to some extent in the surface layer,[24] apparently consistent with the observations in Fig. 2.

It is therefore not surprising that with all the energy effects (chemical, surface, strain, interface) combined in a MD simulation, the apparent ΔH comes out less positive on Ag-covered Cu surface than in the bulk, and more so at elevated temperatures, to allow entropy driven intermixing. It is interesting to observe this phenomenon even at Ag coverages as high as 0.9 ML. Our MD simulations indicate that the free energy reduction due to the alloying of Cu into the top Ag surface layer more than compensates for the free energy increase arising from the mixing of Ag into the first Cu layer. In contrast, further MD simulations show that when two ML's of Ag are deposited on Cu, the apparent ΔH between the two Ag/Cu interface layers is now 6.3 kJ/mol, close to the bulk value. As a result, no alloying significantly beyond the equilibrium solubility is expected and a sharp Ag/Cu interface indeed remained even after long MD runs at 800 K. In other words, enhanced solubility is appreciable only when the Ag/Cu atoms are exposed as part of the free surface. In fact, our energy calculation results at different coverages suggest that the larger the portion of the alloyed layers is on open surface, the less energy cost for intermixing. In addition to coverage, one expects that surface orientation may also affect the apparent ΔH of Ag/Cu: the effect will be larger for surfaces more open than (100) and smaller on more close-packed surfaces.

In summary, we have used MD simulations to monitor the thermodynamic driving force for alloying for Ag deposited on Cu(100). Near RT the driving force available for surface alloying diminishes at high Ag coverages. Compared with the bulk, however, the free surface better accommodates the strains induced by alloying large size-mismatched Ag and Cu, especially at elevated temperatures, effectively reducing the ΔH relative to the bulk value. Our quantitative assessments of the enthalpic as well as entropic contributions show substantial driving force for alloying at moderately elevated temperatures, leading to the observation of pronounced reaction between the reconstructed Ag top layer and the first Cu substrate layer to form substitutional solid solutions with solubilities extended well beyond equilibrium limits.

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[16] $x'_a = x_a/(f\cdot x_b + x_a)$, $x'_b = f\cdot x_b/(f\cdot x_b + x_a)$, where the clustering factor $f = N^c_{ab}/N^i_{ab} (0 < f \leqslant 1)$, N^c_{ab} is the number of unlike a-b bonds, computed from the MD simulation, and N^i_{ab} is the number of a-b bonds in an ideal solution. For example, f is 0.78 for the configuration in Fig. 2.

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