

## Adsorbate-Induced Alloy Phase Separation: A Direct View by High-Pressure Scanning Tunneling Microscopy

Ebbe K. Vestergaard, Ronnie T. Vang, Jan Knudsen, Thorbjørn M. Pedersen, Toshu An, Erik Lægsgaard,  
Ivan Stensgaard, Bjørk Hammer, and Flemming Besenbacher\*

*Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus,  
DK 8000 Aarhus C, Denmark*

(Received 7 May 2005; published 12 September 2005)

The influence of high pressures of carbon monoxide (CO) on the stability of a Au/Ni(111) surface alloy has been studied by high-pressure scanning tunneling microscopy. We show that CO induces a phase separation of the surface alloy at high pressures, and by means of time-lapsed STM movies we find that Ni atoms are removed from the surface layer during the process. Density functional theory calculations reveal the thermodynamic driving force for the phase separation to be the Au-induced compression of the CO overlayer with a resulting CO-CO repulsion. Furthermore, the atomistic mechanism of the process is shown to be kink-site carbonyl formation and evaporation which is found to be enhanced by the presence of Au.

DOI: [10.1103/PhysRevLett.95.126101](https://doi.org/10.1103/PhysRevLett.95.126101)

PACS numbers: 68.35.Rh, 68.35.Md, 68.37.Ef, 68.43.Bc

There is an increasing awareness of the fact that chemical reactivity of bimetallic catalysts can be radically different from the reactivity of either of the elemental component metal catalysts [1–9]. In the past the main focus has been on the class of binary metal systems that form thermodynamically stable, ordered or random bulk alloys. Recently, however, it has been shown that another class of very interesting, so-called surface alloy systems exists that do mix and form alloys in the surface layer, although the constituent metals are bulk immiscible. The prospects of designing novel catalysts with improved chemical properties, both with respect to the overall activity and not least the selectivity, has spurred a lot of scientific interest in alloy systems. It has been demonstrated that we are today approaching an era where knowledge gained from fundamental surface science studies on alloys may lead to the nanoscale design of new and improved high surface area industrial catalysts [8].

One issue, which remains to be addressed is, however, whether such alloy systems are stable when the pressure gap between the idealized, well-controlled low vacuum conditions for typical fundamental model studies and the high gas pressures at industrially relevant catalytical conditions is bridged. Adsorption-induced effects on alloy surfaces have previously been observed. Segregation of the more reactive species in bimetallic alloys has, e.g., been investigated under reaction conditions [10,11], and bimetallic overlayers have been found to exhibit morphological changes upon exposure to adsorbates [12].

Based on an interplay of fast-scanning, high resolution STM and density-functional theory (DFT) calculations we will show in this letter that adsorption-induced phase separation may indeed occur when the surface alloy is exposed to high pressures of a reactive gas. In the past it has been shown that Au atoms alloyed into the topmost layer of Ni(111) significantly modify the reactivity of the neighboring nickel atoms, thereby rendering the AuNi alloy an

interesting candidate for catalytic applications [8,13]. With the fast-scanning capabilities of our high-pressure scanning tunneling microscope (HP-STM) we have studied the AuNi alloy system when exposed to high pressures of CO, and from real-time STM movies we have followed the dynamics of the phase separation. DFT calculations reveal that the underlying atomistic process is the formation of Ni-carbonyls at step edges. The Au atoms are found to accelerate this process owing to an increased CO-CO repulsion at high pressures.

The experiments were performed in a UHV chamber (base pressure  $\sim 1 \times 10^{-10}$  mbar) equipped with a dedicated HP-STM situated in a HP cell attached directly to the chamber. Further details of the HP cell and gas dosing are described elsewhere [14,15]. The Ni(111) crystal was prepared by several sputtering and annealing cycles (2 keV Ar<sup>+</sup> followed by 800 K annealing in UHV for 10 minutes) and characterized by STM in UHV to check the cleanliness. Au was evaporated onto the sample at room temperature (RT) from a home-built evaporator. Under these conditions, Au islands nucleate at the Ni steps, and the Au coverage is easily determined by STM measurements. Alloying of Au into the topmost Ni-layer was subsequently facilitated by annealing the sample to 800 K for 10 minutes. Figure 1(a) shows an example of an STM image of the Au/Ni(111) surface alloy. For clarity, the Au coverage in this particularly chosen image is rather low. Au is imaged as depressions in the alloy as previously described [8]. In all the high-pressure experiments the Au coverage was kept at  $0.3 \pm 0.1$  ML. DFT calculations were performed using a super cell, plane wave (25 Ry) and ultrasoft pseudo-potential approach with exchange-correlation effects described within the revised Perdew, Burke, Ernzerhof (RPBE) form [16].

When the Au/Ni(111) surface alloy is exposed at room temperature (RT) to 1000 mbar of CO, dramatic morphological changes are observed. The surface is observed to be

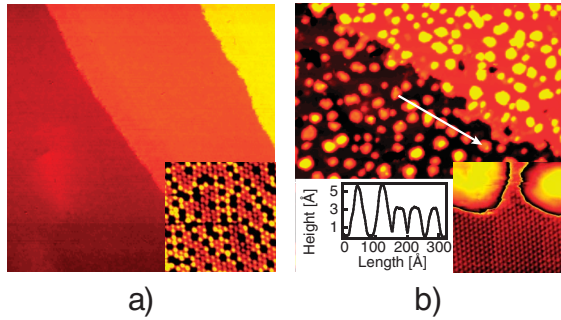


FIG. 1 (color). (a) STM image ( $800 \times 800 \text{ \AA}^2$ ) of Au/Ni(111) after annealing (alloy formation). Inset: Atomic-resolution image ( $50 \times 50 \text{ \AA}^2$ ) of the Au/Ni(111) surface alloy. The Au atoms are imaged as depressions. (b) STM image ( $1000 \times 1000 \text{ \AA}^2$ ) of Au/Ni(111) after exposure to 1000 mbar of CO, in which case the surface is observed to be covered with islands. The line scan (indicated by the white arrow) shows islands of two different heights. Inset: Atomic resolution of an area between the Au islands ( $60 \times 60 \text{ \AA}^2$ ) reveals a clean Ni(111) surface.

covered with small irregular clusters, persisting even after the high-pressure CO is pumped away [See Fig. 1(b)]. A zoom-in on the flat regions between the clusters reveals the clean Ni surface with no Au alloyed into the topmost layer [Inset in Fig. 1(b)] [17], but subsequent annealing at 800 K under UHV conditions restores the original AuNi surface alloy, thus indicating that Au is still present in the surface region after the high-pressure CO exposure. From an analysis of the island height distribution in the STM images we find that most islands have an apparent height of 3.2 Å, while  $\sim 10\%$  have a height of 5.6 Å (See inserted line scan in Fig. 1(b)). The 3.2 Å corresponds well to the height measured for Au islands on Ni(111) after RT evaporation, and are therefore ascribed to monolayer islands of Au. The height difference between the two types of islands is 2.4 Å, which agrees with the step height of Au(111) (2.35 Å), and the taller islands are thus associated with double-layer Au islands. Assuming that the clusters consist entirely of Au, we estimate a Au coverage of  $0.24 \pm 0.04 \text{ ML}$  after high-pressure CO exposure, which is in good agreement with the initial coverage of  $0.32 \pm 0.04 \text{ ML}$  [18]. Based on the above experimental findings we hence conclude that all the observed clusters must be Au clusters, and that the alloy has undergone a complete phase separation.

Lowering the CO pressure to 7–53 mbar, the phase separation slowed down sufficiently that we were able to follow its dynamics by acquiring STM movies. Figure 2 shows a series of STM images picked from such an STM movie acquired at a CO pressure of 13 mbar [19]. The movie reveals that the Au cluster formation starts at the Ni steps. Ni atoms are removed and Au clusters are nucleated and left behind in the wake of the moving step. The process is nonuniform; on each step a large fraction of the Ni atoms is removed from the terrace in certain areas, whereas other areas are nearly intact after a given time. Apparently, the

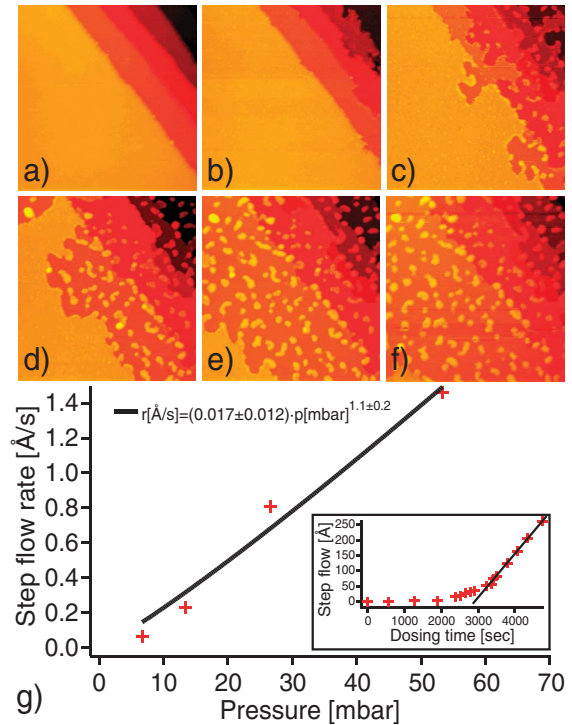


FIG. 2 (color). (a)–(f) STM images ( $1000 \times 1000 \text{ \AA}^2$ ) taken from an STM movie recorded in 13 mbar CO. Time of exposure: (a) 0 min, (b) 25 min, (c) 50 min, (d) 75 min, (e) 100 min, (f) 125 min. (g) Plot of the reaction rate of Ni removal (carbonyl formation) taken from the linear part of step flow graphs (see inset).

Ni atoms removed from the step edge leave the surface since no nucleation of Ni islands is ever observed. The removal of Ni atoms is best explained in a model where Ni-carbonyl molecules are formed and desorb from the surface, as we will discuss below.

To quantify the rate of removal of Ni atoms and the concomitant nucleation of Au clusters, the average movement of the Ni steps (step flow) is determined as a function of time (see inset in Fig. 2(g)). Even though the process is not uniform, this quantity still contains information about the general evolution of the phase separation. The phase separation is characterized by an *incubation* period in which the step edges do not move, followed by a transition to a region where the step edges move with an approximately constant velocity. The incubation time varies largely across the surface, but the final velocity of the step flow can reasonably be used as a parameter for describing the reaction rate on the surface. In Fig. 2(g), the reaction rate (final step flow velocity) is plotted as a function of pressure, and we observe that the rate at which Ni atoms are removed scales as a power law as a function of the CO pressure with a reaction order of  $1.1 \pm 0.2$ , i.e., a linear dependence of the CO pressure within the uncertainty of the data.

The removal of Ni atoms from the step edges does not stop after the completion of the phase separation, and even

on the clean Ni(111) surface (no Au deposited), we find that atoms are removed at high pressures of CO. The step flow on the pristine Ni(111) surface is, however, severely reduced compared to on the AuNi alloy, and a similar quantification of the rate of Ni removal has therefore not been possible.

To track the atomic origin of the AuNi phase separation, we have performed DFT calculations investigating both the thermodynamics and kinetics of the process. In Fig. 3 we present the surface free energy of Ni(111) and the AuNi surface alloyed with different Au loads and CO coverages. In equilibrium, the lowest free energy curve dictates the thermodynamically preferred surface state at a given CO chemical potential,  $\Delta\mu_{\text{CO}}$ , i.e., as a function of the temperature and CO partial pressure [20]. Figure 3 shows that at  $\Delta\mu_{\text{CO}}$  above  $-1.3$  eV, it becomes preferable to phase separate the alloy constituents. The Ni becomes CO covered, while the Au does not (in the calculations, only the bulk cohesive energy of Au is used). Our DFT calculations thus confirm that the phase separation of AuNi should happen for high CO chemical potentials. High potentials can be achieved either by having low temperatures or high pressures. Experimentally, only the latter shows phase separation, possibly due to slow kinetics at low temperatures.

The calculations further reveal the reason for the phase separation; the Au atoms bind the CO about 1 eV weaker than the Ni atoms. On the alloy, the adsorbed CO's thus relocate away from the Au atoms and effectively become slightly compressed on the Ni atoms. The energy of compression can be calculated on Ni(111) by comparing the

stability of the optimum CO structure with that of the compressed structure. At, e.g., 0.5 ML CO coverage, the compression caused by 12.5% Au corresponds to an energy cost of 0.14 eV per CO (= 0.56 eV per Au), which outweighs the calculated 0.33 eV alloying energy of Au in Ni(111).

Inspired by the removal of nickel atoms inducing the phase separation of AuNi at high pressures of CO, a model based on nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ) formation is presented in the following. Nickel carbonyl formation is a well-known process capable of dissolving Ni atoms from Ni surfaces during exposure to high pressures of CO [23–25], and the process is furthermore utilized industrially for the refinement of nickel (the so-called Mond process [26]). The formation of carbonyls has previously been found to occur with a measurable rate at pressures above  $\sim 10^{-1}$  mbar and temperatures below  $\sim 525$  K [23,25], which overlaps the investigated pressure and temperature range in our experiments ( $>7$  mbar, room temperature). Also, steps and defects have been found to play a dominant role for the reaction rate of the nickel carbonyl formation [25], which further corroborates the idea that the observed removal of nickel atoms from step edges in our experiments is correlated with the formation of carbonyl species. A variety of CO reaction orders for carbonyl formation on nickel crystals and powders have been reported in the literature with values ranging from 0.63 to 2.9 [23,24]. Our extracted reaction order of  $\sim 1$  is thus compatible with these earlier findings, and we therefore propose that the phase separation of the AuNi surface alloy occurs because of the formation of nickel carbonyl species at the step edges, and that these species are volatile and leave the surface. Because of the removal of atoms, the step edge moves and Au atoms diffuse along the step edge to form clusters, which are eventually left behind on the new terrace.

The observed incubation time and nonuniformness of the phase separation could indicate that certain specific sites are the only “active sites” for carbonyl formation at the step edges. Au atoms are known from DFT calculations to wet the Ni steps [27], and initially no free Ni step atoms are thus available. We therefore reasonably associate the incubation time with atomic rearrangements to create free low-coordinated Ni sites, e.g., kink sites [25]. To investigate the atomistic mechanism of the subsequent AuNi dealloying and the reason for the Au promotion of Ni removal, the elementary steps of the carbonyl formation have been addressed by DFT calculations. Two series of calculations were performed: kink-Ni removal from a CO covered Ni(754) surface with and without a substituted Au atom. In both cases, the CO coverage is 0.57 ML, adapting the adlayer geometry reported by Eichler [22]. The Au is substituted at a Ni site inside the Ni(111) terrace to model the situation after the initial Au-plated Ni steps have started retracting, meaning that the steps are mainly Ni. The substituted Ni site is chosen to be that of atop CO bonding, and the CO overlayer is rearranged locally at the kink and step sites as to accommodate the CO elsewhere.

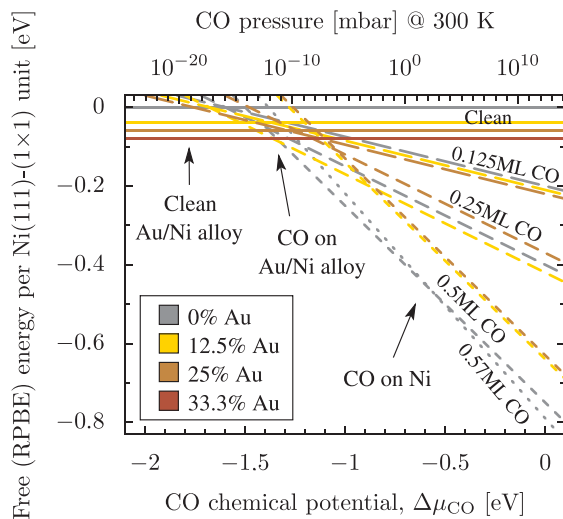


FIG. 3 (color). Free energies of several CO molecules adsorbed on pure Ni and alloyed AuNi surfaces (Au/Ni ratio = 0.125, 0.250, or 0.333). The four horizontal lines represent surfaces with zero CO coverage. At low  $\Delta\mu_{\text{CO}}$  (below approximately  $-1.45$  eV) the clean AuNi alloys (no CO adsorbed) are thermodynamically favored, while CO adsorbed on pure Ni surfaces are favored at higher potentials ( $\Delta\mu_{\text{CO}}$  above approximately  $-1.3$  eV). At  $\Delta\mu_{\text{CO}} \approx -1.35$  eV CO adsorbed on AuNi is favored.

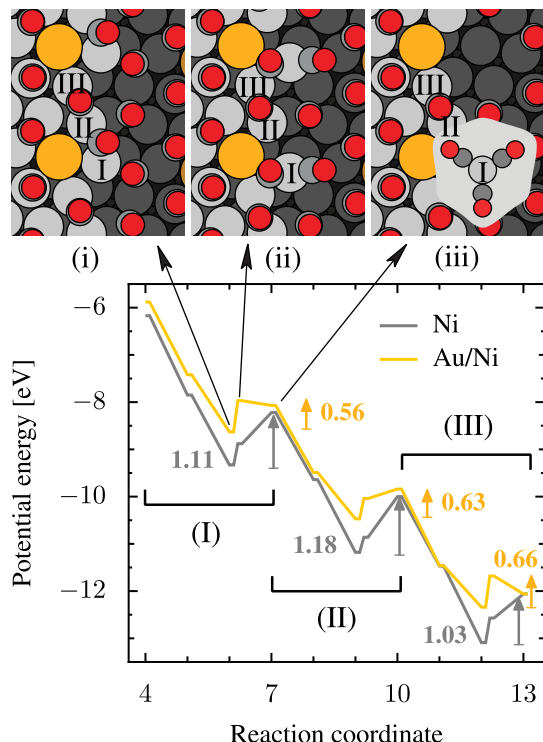


FIG. 4 (color). Top panel: Top view of different configurations during the removal of the first Ni (tagged by I): (i) the fully CO adsorbed surface, (ii) the formation of a  $\text{Ni}(\text{CO})_2$  intermediate, and (iii) the formation and desorption of the  $\text{Ni}(\text{CO})_3$  intermediate. Bottom panel: Potential energy as the three Ni atoms (I, II, and III) are removed on a pure Ni surface (gray) and on a AuNi alloy surface (gold), respectively. Each tick on the  $x$  axis represents a CO taken from the gas phase.

Figure 4 gives the structure and energetics of sequential CO adsorption and  $\text{Ni}(\text{CO})_3$  desorption until three consecutive kink-Ni atoms have been removed. The initial situation is thought to be the surface right after the desorption of a carbonyl from the kink site. The empty CO sites in the CO overlayer are filled with strongly bound CO on Ni and with less strongly bound CO on AuNi. On both surfaces, the Ni can detach slightly ( $\sim 0.8 \text{ \AA}$ ) from the kink site with two CO's residing atop. This rearrangement is associated with a minor energy cost both with and without Au. Now the final state energy of attaching a third CO to this complex and bringing the carbonyl into the gas phase turns out to be more or less the same for pure Ni as for AuNi. However, since the CO's were less strongly bound on the AuNi than on Ni, the reaction energy for the  $\text{Ni}(\text{CO})_3$  formation calculated from the initial state (the fully CO covered surfaces), becomes much larger for pure Ni than for AuNi. This holds true for all three kink-Ni atoms removed, meaning that the result is insensitive to the details of the CO pattern right at the kink sites. The calculations offer a general explanation of the faster carbonyl formation on AuNi, namely, that the CO compression (that originates from the presence of Au) leads to a CO

destabilization that enables more exothermic and hence possibly less activated pathways towards the carbonyl formation. Once  $\text{Ni}(\text{CO})_3$  is desorbed, the formation of  $\text{Ni}(\text{CO})_4$  in the gas phase is associated with a further 1.04 eV energy release.

With our presented high-pressure studies of CO on Au/Ni(111) we have shown an example of chemical attack and destruction of a surface alloy, which only occurs at pressures well above what is usually studied in the UHV-based surface science model systems. Through DFT calculations we have provided evidence for a model explaining the observed phase separation, where Ni-carbonyl formation is responsible for the removal of the Ni atoms in the surface layer.

We acknowledge financial support from the Danish Research Council and computational resources from Dansk Center for Scientific Computing.

\*Corresponding author.

Email address: fbe@inano.dk

- [1] J. Greeley *et al.*, Nat. Mater. **3**, 810 (2004).
- [2] J.R. Kitchin *et al.*, Phys. Rev. Lett. **93**, 156801 (2004).
- [3] F. Buatier de Mongeot *et al.*, Surf. Sci. **411**, 249 (1998).
- [4] J.A. Rodriguez, Surf. Sci. Rep. **24**, 223 (1996).
- [5] R.C. Yeates *et al.*, Surf. Sci. **134**, 729 (1983).
- [6] C. Xu *et al.*, J. Phys. Chem. **98**, 585 (1994).
- [7] C.T. Campbell, Annu. Rev. Phys. Chem. **41**, 775 (1990).
- [8] F. Besenbacher *et al.*, Science **279**, 1913 (1998).
- [9] M. Schmid *et al.*, Phys. Rev. Lett. **70**, 1441 (1993).
- [10] J. Nerlov *et al.*, Appl. Catal., A **191**, 97 (2000).
- [11] E. Christoffersen *et al.*, J. Catal. **199**, 123 (2001).
- [12] K. Pohl *et al.*, Nature (London) **397**, 238 (1999).
- [13] P.M. Holmblad *et al.*, J. Chem. Phys. **104**, 7289 (1996).
- [14] E. Lægsgaard *et al.*, Rev. Sci. Instrum. **72**, 3537 (2001).
- [15] P. Thostrup *et al.*, J. Chem. Phys. **118**, 3724 (2003).
- [16] B. Hammer *et al.*, Phys. Rev. B **59**, 7413 (1999).
- [17] The STM image was obtained at tunneling conditions where the adsorbed CO was swept away by the tip.
- [18] The initial coverage of Au was determined from the step-nucleated Au islands prior to alloying. The small drop in Au coverage arises from bulk diffusion of Au at the initial 800 K annealing during the formation of the alloy.
- [19] The movie can be seen in its full length at <http://www.phys.au.dk/camp/movies/carbonyl.mpg>
- [20] The AuNi surface alloy was composed of a spin-polarized 4-layer Ni(111) slab (two bottom layers fixed). Entropy effects are solely included for gas-phase CO [21]. For the CO overlayers on Ni(111) we have used the most stable structures at various coverages found by Eichler [22].
- [21] K. Reuter *et al.*, Phys. Rev. B **68**, 045407 (2003).
- [22] A. Eichler, Surf. Sci. **526**, 332 (2003).
- [23] P. de Groot *et al.*, Surf. Sci. **94**, 204 (1980).
- [24] K. Lascelles *et al.*, Surf. Sci. **125**, L67 (1983).
- [25] V.K. Medvedev *et al.*, Surf. Sci. **401**, L371 (1998).
- [26] L. Mond *et al.*, J. Chem. Soc. **57**, 749 (1890).
- [27] H.S. Bengaard *et al.*, J. Catal. **209**, 365 (2002).