Composition, structure and stability of surfaces formed by Ni deposition on Pd(111)

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Abstract:

Surface composition and structure of deposited Ni ultrathin films grown on a Pd(111) surface and their thermal stability have been studied using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and scanning tunneling microscopy (STM). In experiments where up to 2 monolayers (ML) of Ni was deposited onto Pd(111) at 300 K, the initial film growth followed a non-ideal layer-by-layer growth mode, in which the majority of the surface was covered by a single atomic layer of Ni, but the second Ni layer started to appear before the first layer was completed. Annealing the Ni/Pd(111) surface to 600 K caused Ni interdiffusion into subsurface layers and the outermost surface was mainly Pd. This structure, designated as Pd-Ni-Pd(111), was not stable in the presence of surface oxygen. Ni segregated to the topmost surface layer to form a (2×2) superstructure after exposing the Pd-Ni-Pd(111) surface at 590 K to 350 L O₂. The oxygen-induced segregation of Ni is consistent with predictions from density functional theory (DFT) calculations.

Keywords:

Bimetallic surface, subsurface monolayer, surface segregation, STM, LEIS, DFT

1. Introduction

It is well known that bimetallic alloys often possess improved catalytic properties, such as higher activity and selectivity towards desirable reactions, than either of the parent metals. This is extremely important for precious transition metal catalysts, like Pt and Pd. Alloying the expensive Pt or Pd with other elements may not only reduce the cost, but also introduce new structures and unique chemical properties. In the past, we have studied the Ni-Pt system extensively and discovered a sandwich-like structure after annealing a Ni-monolayer covered Pt(111) surface to 600 K. This structure, designated as Pt-Ni-Pt(111), contains a subsurface monolayer (ML) of Ni underneath a Pt-rich surface and shows unique chemical properties, such as weaker metal-hydrogen bonding[1, 2], hydrodesulfurization of thiophene at lower temperatures[3], and higher activity and selectivity towards hydrogenation of unsaturated aldehyde[4, 5]. Density functional theory (DFT) confirms that subsurface *3d* transition metals (TMs) (*3d* = Ti, V, Cr, Mn, Fe, Co, or Ni) will broaden the Pt surface *d*-band and therefore reduce the dissociative adsorption energy of H₂ and O₂[6]. The surface properties and reactivities of bimetallic Pt-*3d* TM surfaces and their properties for heterogeneous catalysis have been reviewed recently[7].

Similar to Ni-Pt, the Ni-Pd bimetallic system also shows Pd surface segregation and enhanced activity and selectivity towards hydrogenation of 1,3-butadiene [8-12]. Pd segregation has been observed on a wide range of different crystal faces of Pd-Ni bulk alloys, such as (110)[12-15], (100)[16, 17], and (111)[10, 18]. For example, low energy ion scattering (LEIS) was used to determine that the surface compositions of Pd₁Ni₉₉ and Pd₅Ni₉₅ alloys equilibrated at 870 K were 20 and 50 at.% Pd, respectively[8]. Derry *et al.* [16] observed an oscillatory depth profile of a

Pd₅₀Ni₅₀(100) surface using low energy electron diffraction (LEED), in which the Ni concentration in the first three layers was 20%, 100% and 36%, respectively. Theoretical simulations predict oscillatory depth profiles for all faces [19-21].

In related studies of Ni films deposited on Pd substrates, Granozzi and coworkers investigated Ni ultrathin films on Pd(100)[22-24] and Kleiman's group studied Ni thin film growth on Pd(111)[25, 26] using LEED, X-ray photoelectron diffraction (XPD) and X-ray photoelectron spectroscopy (XPS). After depositing Ni on Pd(111) at room temperature, the (1×1) LEED pattern showed a diffuse background, reported to arise from a random distribution of Ni atoms. Annealing to 300 °C led to a sharp (1×1) pattern, but Ni and Pd XPS intensities did not change much[25]. Although XPD results fit with a model in which part of the surface was comprised of a Ni_xPd_{100-x} alloy with alternating Ni concentrations at each layer, there was no direct evidence to support a subsurface Ni-monolayer structure. In order to testify the sandwich-like subsurface Ni-monolayer structure and to determine the concentration of Ni atoms in the surface layer, additional studies that include the use of LEIS are required, which is sensitive to the outermost atomic layer at a surface.

Surface stability and reconstruction under reactive conditions are also crucial criteria for designing bimetallic catalysts. Granozzi and coworkers showed evidence of CO-induced reconstruction on a Ni/Pt(111) surface, where the monolayer thick Ni films turned into at least two-layer-high islands after exposing to CO[27]. A previous study of Ni/Pt(111) alloy surfaces established that oxygen-induced surface Ni segregation occurred using Auger electron spectroscopy (AES)[28]. In that work, the Ni AES intensity increased and Pt AES intensity

decreased after annealing the Pt-Ni-Pt(111) surface in the presence of O₂. DFT calculations for this system lead to the conclusion that Pt-3d-Pt(111) surfaces are stable under vacuum and hydrogen environments, but thermodynamically unstable with 0.5 ML adsorbed O atoms [28-31].

Regarding oxygen-induced segregation, the situation expected for the Ni-Pd system is not completely clear since Pd has a higher affinity to oxygen than Pt does. This can be seen in the higher desorption temperature for O₂ from low coverage of adsorbed oxygen adatoms on Pd(111) at 840 K[32] than on Pt(111) at 750 K[33]. Stronger Pd-O interactions reduce the driving force for Ni segregation in oxidative environments and may preserve much of a Ni-monolayer subsurface structure, which may be the desired active site for hydrogenation reactions[11], over a wider range of conditions. Therefore, it is also important to characterize the oxygen-induced surface segregation of Ni on Ni-Pd surface alloys.

In order to better characterize the surface composition, structure, and stability of Ni-Pd surface alloys, we have performed experimental and theoretical studies. In this paper, we report results after depositing ultrathin Ni films on a Pd(111) surface and examining its thermal stability and oxygen-induced segregation using AES, LEIS, XPS, LEED, and scanning tunneling microscopy (STM). DFT calculations were used to investigate the thermodynamic stability of the subsurface monolayer structure for bimetallic systems of Pd with Ni and with other 3d TMs.

2. Experimental and DFT methods

Experiments were performed in an ultrahigh vacuum (UHV) system with two connected chambers. The system base pressure was 2.0×10^{-10} Torr. The analysis chamber was equipped for

AES, XPS, LEIS, and LEED, and the STM chamber contained a RHK Technology UHV 300 variable-temperature STM. X-ray excited Auger transition lines (XAES) was recorded for the AES measurements. XPS, XAES and LEIS spectra were taken using a SPECS PHOIBOS 100-mm HSA equipped with a 5-channel multichannel detector (MCD-5). A PHI 14-500 dual anode X-ray source was operated at 15 kV to generate Al K α radiation for XPS and XAES. LEIS was carried out at a scattering angle of 135° using a SPECS IQE-12 ion gun operated to produce a 0.38 nA (48 nA/cm²) He⁺ ion beam at 1.0 keV. The helium discharge pressure measured on the differential pumping port for the ion gun was 2.0×10⁻⁸ Torr while the analysis chamber background pressure was 1.2×10⁻⁹ Torr when performing LEIS. Sputtering from incident He⁺ ions was negligible in the spectra analyzed, which were obtained in 1-3 minutes while the surface composition remained constant after being exposed to the He⁺ beam for 10 min. For STM, tungsten tips were prepared by electrochemical etching W wires (0.009-in dia., 99.5%, ESPI Metals) in a 2 M NaOH solution. The STM was operated in constant current mode with a tunneling bias applied to the sample.

The Pd(111) single crystal (5N purity, polished to 0.5°, Metal Crystals and Oxides LTD) was a round disk with a 6-mm diameter and 1-mm thickness. It was cleaned by repeated cycling between 500-eV Ar⁺ ion sputtering at 1.0 μ A (1.3 μ A/cm²) for 10 min at 300 K and annealing in UHV to 1150 K. This was then followed by treatments using 5×10⁻⁸ Torr O₂ at 800 K for 5 minutes and a final quick flash to 1000 K in vacuum. The surface cleanliness and order were checked by AES, LEIS and LEED prior to each experiment.

Ni was deposited onto the Pd(111) surface at 300 K by thermal evaporation. The Ni

evaporator consisted of a Ni wire (0.1-mm dia., 99.997%, Alfa Aesar) wrapped on a resistively heated W wire (0.5-mm dia., 99.98%, ESPI Metals) surrounded by a stainless steel shield. The chamber pressure while depositing Ni was maintained at 7×10^{-10} to 1.0×10^{-9} Torr after sufficient outgassing of the Ni evaporator prior to deposition. Ni “uptake curves”, in which the Ni signal was monitored for changing Ni deposition times, were taken sequentially, in which the sample was moved between the analyzer position and the Ni evaporator for additional deposition after each data point was obtained.

Annealing experiments were done by heating the crystal to the desired temperature for 2 min and then cooling the sample to 350 K to take the spectra. STM imaging of annealed surfaces was performed in all cases after the sample had been cooled completely to 300 K to reduce thermal drift. For the annealing experiments in the presence of oxygen, the sample was first heated to 600 K and then exposed to a desired amount of oxygen. O_2 exposures are reported herein using units of Langmuir (L: $1 \text{ L} = 1.0 \times 10^{-6} \text{ Torr} \cdot \text{s}$) without any correction for ion gauge sensitivity. Increasing O_2 exposures were obtained by increasing the pressure of O_2 from 1.0×10^{-8} to 2.0×10^{-6} Torr with a constant 100 s exposure time.

For the DFT calculations, the Pd-3d bimetallic surfaces were modeled using density functional theory as implemented by the Vienna *ab-initio* simulations package (VASP) [34-36]. The core electrons of the atoms were described using the ultrasoft Vanderbilt pseudopotentials (US-PP)[37, 38]. The exchange correlation was approximated using the PW91 functional as implemented in the generalized gradient approximation (GGA) [39]. The basis set was comprised of planewaves with an energy cutoff of 396 eV.

The electronic and chemical properties of the $3d$ -modified Pd surfaces were calculated using a 2×2 periodic metal slab with four metal layers. The metal slabs were separated by six equivalent layers of vacuum to minimize electronic interaction between slabs. Two structural configurations were modeled for each Pd- $3d$ system to determine the effect of metal ordering. The first configuration used was a surface $3d$ -Pd-Pd layering in which the $3d$ metal resides in the topmost layer of the slab with the remaining layers underneath composed entirely of Pd(111) atoms. Alternatively, the subsurface Pd- $3d$ -Pd structure was also included, which consisted of Pd atoms in the topmost layer, $3d$ atoms in the second layer, and Pd atoms in the remaining two layers. In both of these configurations, the bottom two layers were frozen at the bulk Pd metal distance of 2.82 Å as previously determined for the PW91 exchange correlation functional[40]. The structure was optimized by allowing the adsorbates and the metal atoms in the top two layers to relax to their lowest energy positions. The reciprocal space was analyzed using a $3\times 3\times 1$ Monkhorst-Pack k -point mesh[41] generating 5 irreducible k -points in the first Brillouin zone. This k -point mesh has been verified to be sufficient as previous studies have shown negligible changes in the trends for higher k -point meshes[29].

These surfaces were calculated in environments of vacuum, hydrogen and oxygen. The vacuum environment was implemented simply without the addition of any adsorbates on the surface of the slab. Hydrogen and oxygen environments were modeled using the lowest energy ensemble resulting in a 0.5 ML coverage of either adsorbate present as adatoms. For the (111) facet, this ensemble was employed by placing a hydrogen or oxygen atom in two of the four possible three-fold hollow sites within the 2×2 unit cell. The total energy of these structures was

minimized until the convergence criteria were reached, which was that the total energy change between ionic steps was less than 0.0001 eV.

The binding properties and predicted segregation energies of the 3d metal were correlated to the *d*-band center of mass for the surface atoms, which was calculated by projecting the resulting planewaves onto spherical harmonic orbitals and analyzing the first moment of the density of states. The density of states was calculated using a Gaussian smearing method between *k*-points and a cut-off radius of 1.5 Å. The *d*-band center of mass reported are all referenced with respect to the Fermi level.

3. Results and discussion

3.1 Ni film growth on Pd(111) at 300 K

Ni was deposited on the clean Pd(111) substrate at 300 K and both AES and LEIS were used to determine the Ni deposition rate and film growth mode. Fig. 1a shows the AES uptake curve using normalized intensities obtained by dividing Ni(848eV) and Pd(330eV) AES intensities after each deposition by the bulk Ni or Pd AES intensities, respectively. The Pd signal decreased and the Ni signal increased for increasing Ni deposition time. A linear growth region can be drawn for the Ni uptake curve, as indicated by the blue dashed line, with a second linear region indicated by the orange dashed line. In the Frank-van der Merwe (FM; layer-by-layer) or Stranski-Krastanov (SK; layer plus island) film growth modes, Ni forms a complete monolayer covering the Pd substrate prior to the formation of the next Ni layer and the Ni signal increases linearly during monolayer deposition. Thus the “break” or change in slope after the first linear region indicates a

coverage of 1 ML Ni. In Fig. 1a, the attenuation of the Pd signal to 0.68 at the “break” point is consistent with a calculated value of 0.71. The measured Ni/Pd AES intensity ratio of 0.13 at this condition is therefore referred as a practical condition of 1 ML Ni.

Fig. 1. Characterization of Ni deposition on Pd(111) at 300 K using (a) AES and (b) LEIS. (a) The Ni(848eV) AES intensity (■, normalized to bulk Ni intensity) increases and the Pd(330eV) AES intensity decreases (●, normalized to bulk Pd intensity) from Ni deposition. (b) The surface Ni concentration determined by LEIS changes with the Ni deposition time. The Ni monolayer concentration can be defined by identifying the change in slope of the Ni curve in (a) or by extrapolating the tangent line in (b) to 1.0. Non-ideal layering causes deviations in both of the AES and LEIS data sets. For the red points in (b), AES of the same surface analyzed by LEIS gave the same Ni coverage, 1.1 ML.

Because the inelastic electron mean free paths for the Ni(848eV) and Pd(330eV) AES lines are 13.2 and 8.4 Å [42], respectively, which correspond to four or more atomic layers, determining the growth mode and monolayer coverage using AES alone can be challenging. LEIS can be used to determine the elements present in only the topmost surface layer, and thus is a powerful probe for identifying the surface Ni coverage. Fig. 1b shows the Ni film growth curve obtained by LEIS in a separate experiment with a different Ni evaporation rate. The surface Ni concentration ($\theta_{\text{Ni}} = 1$ for 100 at. %) shown in Fig. 1b was calculated by

$$q_{\text{Ni}} = \frac{I(\text{Ni})}{I(\text{Ni}) + I(\text{Pd})/\text{r.s.f.}} \quad (1)$$

where $I(\text{Ni})$ and $I(\text{Pd})$ are the Ni and Pd LEIS signals (determined as the peak areas), respectively, and r.s.f. is the relative sensitivity factor for Pd/Ni. This value was determined to be 2.4 from measurements of annealed Ni/Pd(111) surfaces, close to a previously reported value of 2.3 [9, 43]. For ideal FM or SK growth modes, the surface Ni concentration should increase linearly and reach unity when the first monolayer is complete, and remain at that value regardless of the film thickness. This was not observed, as shown in Fig. 1b, where the intensity deviates from the initial slope beyond $\theta_{\text{Ni}}=0.65$, which indicates some non-ideal layer-by-layer growth or alloying. Extrapolating the linear region at low coverages (dashed line), we conclude that deposition of a full monolayer of Ni is achieved at a deposition time of 11 min. In another independent experiment, two surfaces were prepared with a single 4-min deposition and then 8-min deposition of Ni on Pd(111), as shown as red dots in Fig. 1b. The measured Ni concentration by LEIS was consistent with the previous uptake curve data and the small derivation can be attributed to less

CO coadsorption effect. In addition, the latter as-deposited 12 min-Ni/Pd(111) sample had a Ni/Pd AES ratio of 0.14, corresponding to 1.1 ML of Ni as determined by AES, which shows that the monolayer calibration from AES and LEIS are consistent.

Additional evidence of non-ideal layer-by-layer growth is that the surface Ni coverage determined by LEIS does not reach unity even after extended Ni deposition. After 23 min of Ni deposition, LEIS indicates only 85% Ni, while AES shows an apparent Ni concentration of more than 2 ML. This suggests clustering or alloying occurs for thicker Ni films under these conditions.

Fig. 2. STM topographic images after Ni deposition on Pd(111) surfaces at 300 K for three Ni coverages: (a) 0.27 ML, (b) 0.72 ML, and (c) 1.1 ML. Images are all $100 \times 100 \text{ nm}^2$. Imaging conditions were: (a) -1.42 V, 431 pA; (b) -0.96 V, 319 pA; and (c) -2.12 V, 277 pA.

STM was used to image the morphology of Ni films grown on the Pd(111) surface and these results confirm our interpretation of the AES and LEIS results and the non-ideal layer-by-layer growth mode. Fig. 2 shows a series of STM images of Ni-covered surfaces. At low coverage (0.27 ML Ni, Fig. 2a), Ni nucleated to form small islands and was randomly distributed on the Pd

substrate. Line scans establish the height of the islands as a single layer, equal to the height of monatomic Pd step. Much larger Ni islands were generated and spread over the surface at 0.72 ML Ni coverage (Fig. 2b). Pd atoms of the substrate were clearly visible in between the islands and a small amount of second-layer Ni was observed. The 1.1 ML Ni/Pd(111) surface (Fig. 2c) looked like the as-deposited 0.72 ML Ni/Pd(111) surface, but with less gaps between islands and more second-layer Ni on the islands. Because each layer shows different contrast in the STM image, one can count the area of bright and dark spots in order to obtain coverages. Results for the 1.1 ML Ni/Pd(111) surface indicate that the first layer of Ni had 10% vacancies and the second layer coverage was 6%. Thus, the overall Ni coverage was close to one monolayer, which is consistent with the ML designation by AES and LEIS.

In a previous study of Ni/Pt(111) surfaces[1], at 300 K Ni nucleation favored step edges and deposited islands showed a network of fine lines from strain relief of the lattice mismatch of the two metals. However, in the present study of Ni/Pd(111) surfaces, the as-deposited Ni islands exhibited a roundish shape and were distributed evenly on the Pd substrate. No fine lines were observed in any of the images shown in Fig. 2. It could be that the difference in lattice constant between Ni and Pd (3.52 and 3.89) is a little less than with Pt (3.92), so the strain effects are smaller and the dislocation networks might have some critical strain needed to form. However, we also note the use by Kitchin *et al.* [1] of a much slower deposition rate than reported here (0.35 ML/20 min versus 1.1 ML/12 min). Nevertheless, Ni growth on Pt(111) also demonstrated non-ideal layering. A substantial amount of second-layer Ni formed on top of the first layer at 0.7

ML Ni coverage, and at 1.35 ML Ni/Pt(111) a third layer started to appear before the first layer covered the substrate completely.

Another factor in the growth of Ni films is interdiffusion and alloy formation. Gambardella *et al.* studied Ni growth on a vicinal Pt(111) surface[44] and observed Pt-Ni exchange at a temperature less than 300 K on a Pt(997) substrate. The exchange process happens on both terraces and step edges, but favors the step edges since atoms there have lower coordination number and are less stable than at terrace sites. The Pd(111) sample studied herein has a high step density, with an average terrace size of 20 nm. Therefore it would not be surprising if a similar Pd-Ni exchange process occurred at 300 K. However, in our STM images Ni was not distinguished from Pd atoms. On the Ni/Pt(997) surface, LEED was used to observe the formation of a (2×2) alloy superstructure caused by Pt-Ni exchange at 300 K[44]. In our studies on Pd(111) at 300 K, Ni deposition only caused the Pd(111) (1×1) LEED pattern to be more diffuse and less intense; no ordered alloy structure was observed using either LEED or STM. In addition, no chemical shift of either Ni or Pd core levels was detected by XPS after Ni film deposition. Still, as-deposited Ni islands shown in Fig. 2a cover 35% of the image, higher than the Ni concentration deduced from LEIS measurements, 20%. We attribute this discrepancy to mostly an experimental limitation of a small amount of CO coadsorption, which has a strong effect on intensities in LEIS. But there may also be a small amount of Ni exchanged with Pd to form a surface alloy at 300 K.

3.2 Thermal stability of ultrathin Ni films on Pd(111)

Thermal stability of Ni ultrathin films on a Pd(111) substrate was examined by AES and LEIS after annealing 1ML- and 2ML-Ni/Pd(111) surfaces from 300 to 800 K in 50 K intervals. Fig. 3 illustrates that the surface Ni concentration as monitored by LEIS decreases with increasing temperature much more than that by AES, as expected. LEIS of 1ML-Ni/Pd(111) indicates 70% Ni at 300 K and this value decreases to 10% after annealing to 500 K, as shown in the red curve in Fig. 3b. The AES Ni/Pd ratio (red curve in Fig. 3a) decreases by only 20% after annealing to 500 K. Since LEIS only detects the topmost surface layer, we conclude that most Ni leaves the topmost surface layer but remains in the near surface region after annealing to 500 K. This is consistent with a “sandwich” structure denoted as Pd-Ni-Pd(111) in which there is a relatively large concentration of Ni in the second, subsurface layer under these conditions. A sharp (1×1) LEED pattern, identical to that for the clean Pd(111) surface, was observed after annealing 1 ML Ni/Pd(111) to 500 K, which also supports surface Pd segregation.

Fig. 3. Thermal stability of 1 ML- and 2 ML-Ni/Pd(111) surfaces as probed by the (a) Ni/Pd AES ratio and (b) LEIS Ni surface concentration.

Heating the 1 ML-Ni/Pd(111) sample to 800 K caused an additional decrease in the surface Ni coverage to 6% Ni in LEIS and caused the Ni/Pd AES ratio to decrease to about 1/3 of its initial value at 300 K, which indicates an additional loss of surface Ni atoms and that subsurface Ni diffused deeper into the Pd substrate. Thus, heating to 800 K causes most Ni atoms to diffuse into the bulk of the Pd with only a small amount of Ni left in near surface region and a nearly pure Pd topmost surface layer.

Annealing data for a surface with a higher initial Ni coverage of 2 ML is shown in the two black curves in Fig. 3. Both the AES Ni/Pd ratio and the Ni concentration from LEIS decreased gradually with increasing temperature above 300 K, with the largest changes again occurring near 500 K. A small amount of CO desorption near 450 K may also cause some small changes. The surface Ni concentration determined by LEIS is always much higher at a given temperature compared to the 1ML Ni film, decreasing to 40% after annealing to 550 K, and 30% after 600 K, but then decreases finally to again less than 10% after annealing to 800 K. Ni concentrations in the near-surface region determined by AES from these surfaces are also higher than those after annealing the 1 ML-Ni/Pd(111) films to similar temperatures. These results for annealing 1 ML- and 2 ML-Ni/Pd(111) surfaces from 300 to 800 K are consistent with previous reports [25, 26].

Fig. 4. STM topographic images of Ni/Pd(111) surfaces after annealing to 600 K for three initial Ni depositions: (a) 0.27 ML, (b) 0.72 ML, and (c) 1.1 ML. Images are all $100 \times 100 \text{ nm}^2$. Imaging conditions were: (a) -0.98 V, 396 pA; (b) -1.04 V, 374 pA; and (c) -0.316 V, 520 pA.

Heating accelerates diffusion and intermixing of Ni and Pd atoms and this leads to a surface morphology change. Fig. 4 shows STM images of the same surfaces characterized in Fig. 2 after being annealed to 600 K. At low coverage (Fig. 4a, 0.27 ML), islands now appear at step edges or as larger features on terraces. The second case is more dominant on wider terraces, where islands over 20 nm in diameter were observed. On narrower terraces, no large islands were observed, but the number of individual islands was greatly reduced. This is reasonable since atoms on narrow terraces have a higher possibility of diffusing to step sites where they build up at the step edges and cause irregular step edge shapes. Atoms on wide terraces, traveling the same distance, more readily diffuse to the edge of an adjacent island and stabilize there before they reach the step edges of the substrate.

After annealing a sample with 0.72 ML Ni/Pd(111) to 600 K (Fig. 4b), step growth was more extensive causing large changes in the step morphology, in some cases connecting with holes in

the middle. The appearance of the annealed 0.72 ML-Ni/Pd(111) surface was quite flat and uniform, similar to the annealed 0.70 ML-Ni/Pt(111) surface[1]. Although we could not discriminate Ni from Pd atoms by STM in these experiments, LEIS indicates only 7% Ni in the topmost surface layer for this image, suggesting that Ni-Pd interdiffusion has taken place and the observed irregularly shaped terraces are mainly Pd.

After annealing 1.1 ML-Ni/Pd(111) to 600 K (Fig. 4c), the surface shows flat, ordered terraces in which the step density and terrace width are close to that of the clean Pd(111) surface, even though the step edges are slightly less straight. There are some small (1-3 nm) islands present near the step edges, but they account for less than 1% of the total surface area.

We also performed STM imaging after annealing each of the surfaces from Fig. 4 to 800 K (not shown) and the images were nearly the same as those for clean Pd(111). Most of the Ni atoms have diffused deep into the substrate and Pd segregates strongly to the surface layer, and therefore the surface morphology is unaffected by initial Ni coverage after heating to 800 K.

3.3 Oxygen-induced surface segregation

Oxygen-induced Ni segregation was studied by using LEIS, AES, XPS and STM. A 1 ML-Ni/Pd(111) sample was first annealed to 600 K to produce a Pd-Ni-Pd(111) structure and then exposed to 1.0×10^{-8} to 2.0×10^{-6} Torr O_2 by backfilling the chamber with the sample temperature held at 590 - 620 K. All spectra were taken after the sample was cooled to < 350 K after each exposure. Fig. 5 shows the influence of O_2 exposure at 590 K on the Pd, Ni, and O

LEIS intensity. Surface oxygen causes the O LEIS signal to quickly increase from near zero to a saturation value after 5-L O₂ exposure, corresponding to the maximum O concentration reached even after several hundred Langmuir O₂ exposure. Oxygen bonding with both Pd and Ni atoms is implied since with higher O₂ exposures, the O signal remains the same while Ni segregates to the surface, as indicated by the increasing Ni and decreasing Pd signals in LEIS. The size of the Ni LEIS peak increase is smaller than that of the Pd LEIS peak decrease in part because of the higher LEIS sensitivity to Pd than Ni. After a 200 L O₂ exposure, obtained with the sample at 590 K for a little over 6 min, both Ni and Pd peak intensities reached constant values with the Pd peak about the same size as the Ni peak. Given the relative sensitivity factor of Pd/Ni = 2.4, this corresponds to a Ni/Pd surface concentration of about 3:1. Therefore, O₂ exposure under these conditions does not fully recover the Ni from the subsurface region and about one-fourth of the Ni deposited prior to oxygen exposure migrates to the Pd bulk. We propose that the final surface is predominately oxygen adatoms adsorbed at Ni sites and is designated as O/Ni/Pd(111) hereafter.

Fig. 5. LEIS intensity change arising from O₂ exposures on the 600 K-annealed 1ML-Ni/Pd(111) surface at 590 K. The O (●) and Ni (▲) LEIS intensities are displayed on the left side ordinate, while the Pd LEIS intensity (■) is displayed on the right side ordinate.

No chemical shift of either Ni 2p_{3/2} (852.5 eV) or Pd 3d_{5/2} (335.0 eV) peaks in XPS was observed after the formation of the O/Ni/Pd(111) surface, as shown in Fig. 6. The Pd 3d peaks after exposing to 500 L O₂ at 590 K decrease in intensity, as more clearly shown by the difference spectra. These peaks are relatively insensitive to these surface changes because of the large contribution from the Pd bulk metallic phase. The Ni 2p_{3/2} peak, obtained after annealing the 1-ML Ni/Pd(111) surface to 600 K, was also not strongly altered after exposing to 500 L O₂ at 590 K, as indicated by the difference spectrum. We can contrast this result to that in our previous study of oxidation of Sn-Pt surfaces [45], where both metallic and oxidized Sn 3d_{5/2} peaks were observed after a 5-ML Sn/Pt(111) surface was exposed at 300 K to 500 L O₂. Maire *et al.* [46] reported that the Ni 2p_{3/2} peak shifted from 852.8 to 854.5 eV after exposing a Ni_{0.7}Pt_{0.3} alloy single crystal at 573 K to 0.1 Torr O₂ for 5 h (1.8×10⁹ L). Thus it is not surprise that a 500 L O₂ exposure on the Pd-Ni-Pd(111) surface at 590 K causes Ni surface segregation but does not lead to a Ni oxidation, and much more extensive oxidation conditions must be applied in order to fully oxidize the Pd-Ni-Pd(111) surface.

Fig. 6. Ni 2p and Pd 3d XPS spectra of 600 K-annealed 1ML-Ni/Pd(111) surfaces taken before and after exposing to 500 L O₂ with the sample held at 590 K. The spectra indicate that both Ni and Pd remain unoxidized. Difference spectra shown at the bottom of each panel were obtained by subtracting the spectra before O₂ exposure from the spectra after 500 L O₂ exposure.

A (2×2) LEED pattern first appeared after 60 L O₂ and became brighter after 100 L O₂ exposure on the Pd-Ni-Pd(111) surface at 590 K. Fig. 7 shows STM images and the corresponding LEED pattern of a O/Ni/Pd(111) surface produced by annealing the 1-ML Ni/Pd(111) surface to 600 K and then exposing this surface at 590 K to 350 L O₂. Fig. 7a displays a large flat terrace that has dark spots covering about 5% of the surface area. Line profiles of the dark spots indicate that they are holes with a depth of a single atomic layer (1.2 Å). Atomically resolved images shown in Fig. 7b confirm the existence of a (2×2) superstructure. A (2×2) unit cell, superimposed on the image using white lines, has a length of 5.6 Å, twice that of the nearest neighbor distance of 2.8 Å in Pd(111).

In addition, heating the (2×2)-O/Ni/Pd(111) surface to 600 K in vacuum causes oxygen desorption and diminishes the intensity of the (2×2) LEED pattern. Heating the (2×2)-O/Ni/Pd(111) sample at 600 K with 2×10^{-8} Torr CO for 10 min completely removes surface oxygen and causes the surface to revert to the Pd-Ni-Pd(111) structure. This conclusion is based on the LEIS curve taken from this surface, which shows that the topmost surface layer was free of Ni, and the amount of Ni left in the subsurface, as examined by AES, was close to that found for the Pd-Ni-Pd(111) surface.

Fig. 7. (a) and (b) STM topographic images of a (2×2)-O/Ni/Pd(111) surface formed by annealing 1.1 ML Ni/Pd(111) to 600 K and then exposing at 590 K to 350 L O₂. (a) Large-scale image obtained for an area of 100×100 nm². (b) Small-scale image for an area of 6×6 nm². The (2×2) unit cell is superimposed on the STM image using white lines. STM imaging conditions were: (a) -144 mV, 0.50 nA and (b) 25.8 mV, 3.17 nA. (Top right) LEED pattern obtained for the surface imaged in (a) and (b). (Bottom right) Height profile of the white line in upper right corner of image (a).

Fig. 8. Effect of O₂ exposure on Pd-Ni-Pd(111) at 560, 590 and 620 K on the Ni/Pd AES ratio.

The Ni/Pd AES ratio from the prepared Pd-Ni-Pd(111) and Ni-Pd-Pd(111) surfaces was assigned to be 0 and 1, respectively, in order to compare to ref. [29].

In order to compare to previous studies of Ni/Pt(111)[29], we also examined the O₂-induced Ni surface segregation using AES and the results are shown in Fig. 8. The surface with a 1-ML Ni film (Ni-Pd-Pd(111)) was first annealed to 600 K to form the subsurface structure (Pd-Ni-Pd(111)) and then exposed to O₂ at different temperatures. The extent of Ni segregation was indicated by the normalized Ni/Pd AES ratio, which was calculated by assigning the Ni/Pd AES ratio from the Pd-Ni-Pd(111) and Ni-Pd-Pd(111) surfaces to be 0 and 1, respectively[29]. Fig. 8 shows that the Ni/Pd AES ratio increases as Ni segregates to the surface when exposing to oxygen and this segregation is accelerated at higher reaction temperatures. The normalized Ni/Pd AES ratio

obtained from surfaces kept at 590 and 620 K reach maxima of 0.47 and 0.41, respectively, after exposing to 200 L or higher O₂, consistent with our LEIS results. The surface exposed at 560 K shows much weaker Ni enhancement. After 200 L, the Ni/Pd AES ratio only increased by 20%, which is less than one-half the value seen for the surface at 590 and 620 K. In another experiment at 500 K (not shown here) the Ni/Pd AES ratio only reached 0.2 after exposure to 500 L O₂. An Arrhenius plot using data from 560 - 620 K was used to estimate an activation barrier for Ni surface segregation of $E_a \sim 15$ kcal/mol.

Comparing this data to that from Ni/Pt(111), the magnitude of O₂-induced Ni segregation for the Ni/Pd(111) system is smaller. The normalized Ni/Pt AES ratio obtained by the same method reached a value of 0.9 after oxidizing the Pt-Ni-Pt(111) surface at 620 K with 200 L O₂ [29]. Yet calculated activation barriers for Ni surface segregation on the Pt-Ni-Pt(111) surface were reported as $E_a = 27$ kcal/mol above 600 K and $E_a = 17$ kcal/mol at 500-590 K. For the Ni/Pd(111) system, Ni never fully segregated to the topmost surface as indicated by both LEIS and AES, but this behavior does not seem to be due to an increase of the activation barrier for Ni surface segregation.

3.4 DFT calculation of the stability of Pd-Ni structures in vacuum and with adsorbed oxygen

DFT calculations were performed to determine the thermodynamic stability of Pd-Ni structures, as well as trends upon alloying of Pd with other 3d transition metals (TMs), where 3d = Ti, V, Cr, Mn, Fe, Co, and Ni. The total energy of the surface 3d-Pd-Pd(111) structure was

compared to the subsurface Pd-3d-Pd(111) structure in vacuum (without adsorbate) along with 0.5-ML coverages of atomic hydrogen and oxygen. The surface and subsurface configurations are two extreme structures possible for these alloys. It has been predicted previously that the intermixed configurations that have both Pd and 3d atoms within each layer exhibit properties that fall within these two layering extremes[30]. The predicted thermodynamic potential for segregation, ΔE_{seg}^A , for the 3d admetal to interchange from a subsurface layer to the surface structure with adsorbate A was calculated as follows:

$$\Delta E_{seg}^A = \frac{E_{A/3d-Pd-Pd} - E_{A/Pd-3d-Pd}}{M} \quad (2)$$

where $E_{A/3d-Pd-Pd}$ is the total energy of the surface structure with adsorbate A , $E_{A/Pd-3d-Pd}$ is the total energy of the subsurface structure with adsorbate A , and M is the total number of Pd-3d metal pairs in the unit cell. For a 2×2 unit cell, there are four Pd-3d metal pairs between the top two layers resulting in $M = 4$. Within this definition, a positive number for ΔE_{seg}^A predicts that the subsurface structure is thermodynamically preferred over the surface structure.

The calculated thermodynamic driving potential for segregation of the Pd-3d systems is shown in Fig. 9 for the environments of vacuum (no adsorbates), 0.5-ML H, and 0.5-ML O. These segregation energies are correlated with the difference in d -band center (always used here as denoting the DOS-weighted d -band center), $\Delta \varepsilon_d$, between the two clean slab configurations.

This difference in the d -band center was calculated as shown in Eq. (3)

$$\Delta \varepsilon_d = \varepsilon_d^{3d-Pd-Pd} - \varepsilon_d^{Pd-3d-Pd} \quad (3)$$

where $\varepsilon_d^{3d-Pd-Pd}$ is the d -band center calculated for the top four 3d atoms in the 3d-Pd-Pd structure and $\varepsilon_d^{Pd-3d-Pd}$ is the d -band center calculated for the top four Pd atoms in the

Pd-3d-Pd subsurface structure. It has been shown previously that the segregation potential for a number of systems correlates linearly with the difference in d -band center[30].

Fig. 9. Thermodynamic potential for segregation from the subsurface to the surface configuration for Pd-3d systems in vacuum, with 0.5 ML H, and with 0.5 ML O correlated to the difference in d -band center of the adsorbate free surface and subsurface structures. The specific Pd-3d system corresponding to each column of points is labeled along the top of the graph.

Fig. 9 shows that for all of the Pd-3d systems, the subsurface Pd-3d-Pd structure is thermodynamically preferred in vacuum and when 0.5 ML of H adatoms are present. However, the surface 3d-Pd-Pd configuration is predicted to be thermodynamically preferred if 0.5 ML of O adatoms are present. Pd-Ni is predicted to have the smallest driving potentials in all three

environments whereas Pd-Ti is predicted to have the largest driving potentials. This is similar to other late transition metal host alloys, such as Pt-3d systems.

In vacuum, this trend can be understood as optimizing the delocalization of electron density on the terminated face. Since Pd is an element in the 4d row of the periodic table, the *d* electrons are more delocalized for these atoms than for the 3d atoms. This difference in the delocalization becomes more pronounced as the comparison is shifted from Pd-Ni to Pd-Ti. This may explain why the thermodynamic driving potential to form the subsurface Pd-3d-Pd structure increased as the 3d metal is switched from Ni to Ti. With adsorbates, the thermodynamic driving potential is a balance of two terms, the intrinsic segregation potential in vacuum and the difference in adsorbate-substrate binding energies between the two configurations[30]. This can be expressed as follows:

$$\Delta E_{seg}^A = \Delta E_{seg}^{vacuum} + \frac{NS}{Mn} \Delta BDE_A \quad (4)$$

where ΔE_{seg}^{vacuum} is the thermodynamic driving potential for segregation without adsorbates, ΔBDE_A is the difference in binding energies of adsorbate *A* between the two configurations, *N* is the adsorbate coverage in ML (0.5 in this paper), *n* is the number of adsorption sites required per adsorbate (*n* = 2 for dissociative adsorption in this paper), *M* is the number of Pd-3d metal pairs in the top two layers (*M* = 4 in this paper) and *S* is the number of possible adsorption sites of specific type per unit cell (there are four 3-fold fcc hollow sites per 2×2 unit cell considered in this paper). The difference in binding energy is calculated as $\Delta BDE_A = BDE_{A/3d-Pd-Pd} - BDE_{A/Pd-3d-Pd}$. The binding energy for 0.5 ML coverage was calculated as

$BDE = E_{A/surface} - E_{surface} - E_{A_2}$, where $E_{surface}$ is the total energy of the surface without

adsorbates and E_{A_2} is the total energy of the diatomic adsorbate (H_2 and O_2) in the gas phase.

For weakly binding adsorbates, such as hydrogen, the difference in binding energy between the two configurations is smaller than the intrinsic segregation potential in vacuum. This results in the subsurface $3d$ structure remaining thermodynamically preferred with 0.5-ML H. On the other hand, with strongly binding adsorbates that have more overlap with d orbitals, such as oxygen, the difference in binding energy between the two configurations is larger than the intrinsic potential in vacuum. This results in the thermodynamically predicted configuration being the surface $3d$ configuration with 0.5-ML O. This prediction is consistent with the experimentally observed oxygen-induced Ni segregation from the Pd-Ni-Pd(111) subsurface structure.

4. Conclusions

The growth of Ni on Pd(111) at 300 K is close to a layer-by-layer growth mode, in which the deposited Ni film forms islands with monatomic height that are randomly distributed on the surface. Non-ideal layering causes a second layer of Ni to form before the first layer is completed. Annealing an as-deposited 1-ML Ni/Pd(111) surface to 600 K causes nearly all surface Ni atoms to leave the topmost surface layer and to concentrate in the near subsurface region, as suggested by comparing the extent of Ni reduction in LEIS and AES results. This is the first direct evidence to support the oscillating depth profile predicted previously by theoretical calculations for Ni-Pd alloys and is broadly consistent with the previously proposed subsurface structure in Ni-Pt systems. STM results show that Ni-Pd interchange occurs with annealing at elevated temperatures and the morphology of annealed surfaces (the subsurface structure) depends on the initial Ni

coverages. At low initial Ni coverages, the surface shows bigger but less islands in the middle of terraces after annealing. At medium initial Ni coverages, islands are coalesced, but cannot cover the entire substrate and so “holes” revealing the Pd substrate surface are still visible. At monolayer initial Ni coverage, complete flat terraces with wandering “curvy” step edges are generated after annealing to 600 K.

Exposing a Pd-Ni-Pd(111) sample at 600 K to O₂ causes Ni subsurface atoms to segregate to the surface. Oxygen initially adsorbs and bonds with Pd at the surface and gradually induces Ni segregation at 600 K as O₂ exposures increase. After 200 L O₂ with the sample held at 590 K, LEIS indicated that 75% of the topmost surface was covered by Ni and O, which has a (2×2) superstructure as revealed by LEED and STM. However XPS showed no significant chemical shift for either Pd or Ni. Therefore, we propose that this (2×2) layer is formed by adsorbed oxygen adatoms. This adsorbed oxygen can be facilely removed by reaction with CO at 600 K.

DFT calculations indicate that the Ni-subsurface configuration, denoted as Pd-Ni-Pd(111), is thermodynamically stable in vacuum and in the presence of 0.5-ML adsorbed H atoms, whereas the Ni-Pd-Pd(111) surface configuration is more thermodynamically stable when 0.5 ML O adatoms are adsorbed. This is a general trend for a Pd substrate and other 3d TMs. The thermodynamic potential for segregation from the subsurface to the surface configuration can be correlated to the Pd-3d d-band center shift between subsurface and surface configurations. Pd-Ti is predicted to have the largest and Pd-Ni the smallest driving potentials for O-induced segregation.

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