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Photoemission microscopy study of the temperature evolution of a Pd film deposited on a polycrystalline Ni substrate

A. W. Potts and G. R. Morrison
King's College London, Department of Physics, Strand, London WC2R 2LS, United Kingdom

A. Barinov, L. Gregoratti, and M. Kiskinova
Sincrotrone Trieste, Area Science Park, SS14-Km163.5, 34012 Basovizza, Trieste, Italy

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We have previously reported a study on the nature of a submonolayer deposit of Pd on polycrystalline Ni. It was shown, using photoemission microscopy, that at 300 K the amount of Pd depended upon the crystal structure of a particular surface grain. Pd was shown to be present on the surface as adsorbed Pd and as a Pd/Ni alloy. Here we report an extension of our original experiments to measurements at different temperatures. It is shown that at 620 and 700 K, stable but different distributions are obtained. It is also observed that the proportion of alloyed to adsorbed Pd depends not only upon the grain structure but also upon the anneal conditions.

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I. INTRODUCTION

In a recent paper we reported the study of a polycrystalline Ni surface onto which approximately one-half monolayer (ML) of Pd had been deposited.[1] All measurements were carried out at room temperature. The principle means of study was the scanning photoelectron microscope (SPEM) on the ESCA microscopy beamline at the Elettra synchrotron. This was supplemented by measurements using a low-energy electron microscope (LEEM) and by micro-low-energy electron diffraction (μ-LEED). As expected,[2] it was shown that the crystal grains on the polycrystalline surface exhibited different attractions for Pd atoms, resulting in local variations in the surface concentration. It was also shown that the surface Pd existed in two forms, interpreted as an adsorbed form and an alloyed form, and that the relative proportions of these also depended upon the crystal grain orientation. Here we have extended our study to include the effects of annealing on the surface.

The nature of the Pd on a Ni surface has attracted considerable interest because, following annealing, such surfaces can show substantially enhanced catalytic activity for hydrogenation reactions.[3–7] Pd-rich Ni surfaces can be produced either by direct evaporation of Pd onto prepared Ni surfaces or through surface segregation resulting from the annealing of bulk alloys. The surface Pd concentration and thermal treatment have been shown to be important considerations in defining the catalytic activity of the surface[3,4] and it is important to know not just the amount of Pd on the surface, but also the form in which it is present.[5–8] It has been shown through a combination of scanning tunneling microscopy (STM) and LEED that Pd is present on a Ni(110) surface partly as small islands of Pd and partly as a Ni/Pd alloy formed at surface steps.[5] While single-crystal studies are important for such determinations,[3,8] it is also important to understand how Pd films deposited on a polycrystalline Ni substrate evolve during the annealing process, since such surfaces are likely to be close to the form of real catalysts used for hydrogenation reactions.

II. EXPERIMENTAL SETUP

The measurements reported here have been performed at the ESCA microscopy beamline of the Elettra synchrotron light facility in Trieste, Italy. The SPEM installed on that beamline produces surface images in terms of the photoelectron signal from particular atomic shells with a spatial resolution of 150 nm and a photoelectron energy resolution of 0.5 eV. Detailed photoemission spectra can be recorded by positioning the focused x-ray probe at chosen locations on the sample surface. The photon energy used for the measurements reported here was 500 eV, and imaging was carried out in terms of the Pd 3*d* signal and Ni 3*p* signal. A detailed description of the experimental setup and procedures used has already been given.[1,9]

The Ni sample in these measurements was produced from commercial 99.98% pure foil 0.25 mm thick. To preserve the polycrystalline nature of the foil but to ensure a flat surface, the foil was compressed against a polished Si wafer using a hydraulic press. It was then cleaned under UHV conditions by several cycles involving heating at 900 K in a 10^{-6} mbar oxygen atmosphere, followed first by Ar ion bombardment and then by annealing at 1100 K. The clean surface was shown to be C and O free by Auger electron spectroscopy, and, after Pd deposition, by the photoelectron spectra recorded with the sample mounted in the microscope. The Pd deposition was performed from 99.99% pure rod with a commercial electron-bombardment, water-cooled evaporator. The amount of deposited Pd was 4×10^{14} atoms cm^{-2} or around 0.5 ML. Annealing temperatures were measured with a chromel/alumel thermocouple welded to the sample itself.

In a previous study of this sample at room temperature,[1] it was shown that the Ni 3*p* photoelectron signal essentially mapped the topography of the Ni surface and that the image was not sensitive to the coverage of Pd studied here. It was found that dividing the Pd 3*d* photoelectron signal from a Pd 3*d* image by the Ni 3*p* photoelectron signal from a Ni 3*p* image of the same area, on a pixel-by-pixel basis, produced

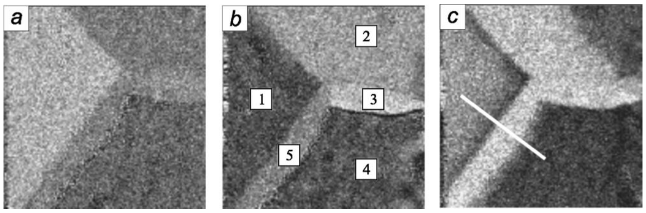

FIG. 1. Images of the selected Ni surface area in terms of the Pd $3d$/Ni $3p$ intensity ratio for various temperatures and anneal times. The area scanned is $64 \times 64\ \mu m^2$. (a) After room-temperature deposition of Pd, (b) after 10 min annealing at 620 K, and (c) after 70 min annealing at 700 K.

an image reflecting the distribution of surface Pd. The use of Pd/Ni ratio imaging to map the relative surface concentration of Pd on the polycrystalline Ni surface has again been adopted here.

III. RESULTS

The Pd/Ni sample was annealed at 620 and 700 K for total periods of 10, 30, and 70 min. Annealing at 700 K was carried out on the sample previously annealed at 620 K. Thermocouple measurements showed that the sample did not reach the specified annealing temperature until about 3–4 min after the nominal start of the annealing time. The conditions under which the most significant changes in the surface Pd concentration occurred, as indicated by the Pd/Ni ratio images, are shown in Fig. 1. The Pd/Ni maps recorded after 30 and 70 min annealing at 620 K do not differ substantially from those taken after 10 min, and the same pattern of behavior is observed for the three anneals at 700 K. As previously discussed,[1] the surface Pd concentration (as indicated by the Pd/Ni ratio) is influenced by the surface grain structure, so that each grain is well defined in the ratio image. This concentration is changed by annealing at 620 K for ≈10 min. As the graph in Fig. 2 shows, the ratio drops significantly on grains 1 and 4, is almost constant on grain 5 and shows a slight increase for grain 2. Further annealing at 700 K results in a recovery in the surface concentration on grain 1, while the concentration on grain 4 continues to decline. Grains 2 and 5 both show overall increases in their surface Pd concentrations. The Pd/Ni ratios given in Fig. 2 are the result of averaging over an area within each grain. A LEEM study of the same sample before Pd deposition showed identical surface grain structure, and the LEED analysis of each grain performed at the Elettra facilities[1] indicated different crystallographic orientations of the visible grains in Fig. 1, although unambiguous assignments were not possible because of the quality of the diffraction patterns.

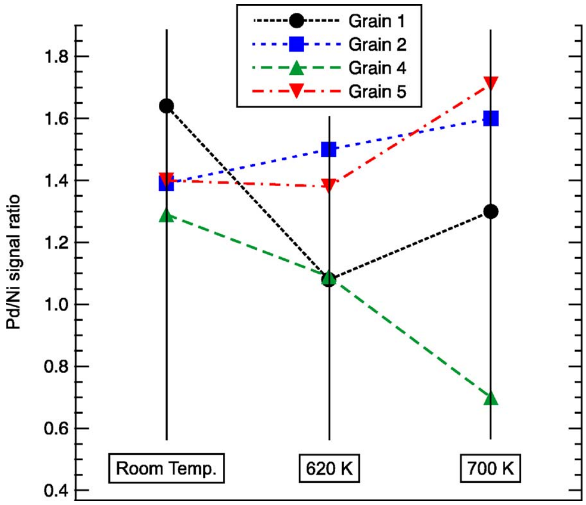

FIG. 2. (Color online) A graph showing relative variations in the Pd/Ni intensity ratios for the different grains, and hence the relative variation of Pd concentration.

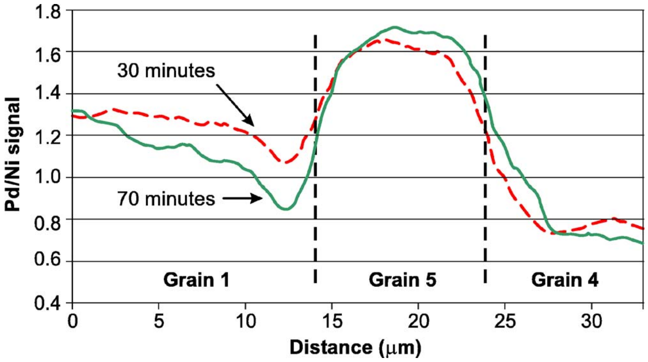

FIG. 3. (Color online) Intensity profiles along the line shown in Fig. 1(c), across grains 1, 5, and 4, for Pd/Ni ratio images taken after annealing at 700 K for 30 and 70 min.

There are changes in addition to the simple intensity changes in the established grain structure observed after the 620 K anneal. The image in Fig. 1(c) shows the development of a darkened (low Pd concentration) region in the top right-hand corner of the image of grain 2. This feature was apparent in all images taken after annealing at 700 K, but in none of the images after the 620 K anneal. The boundary between the two regions of grain 2 is rather more diffuse than observed between other grains in the area shown, but appears to be a real surface effect, possibly associated with restructuring of the Ni surface at the higher temperature. Unfortunately, the results taken during our experimental period at Elettra did not permit this effect to be fully investigated.

A further effect is evident in images recorded after annealing at 700 K. This is the apparent depletion of Pd at the boundary of grain 1, and occurs on the approach to both grain 2 and grain 5. The effect develops with anneal time and is clearly visible in the image in Fig. 1(c). In Fig. 3, intensity profiles for Pd/Ni ratio images recorded after annealing for 30 and 70 min at 700 K [taken along the line indicated in Fig. 1(c)], show the difference in behavior between the 1-5 and 5-4 boundaries. While there is no obvious depletion at the 5-4 boundary, the depletion at the 1-5 boundary increases with annealing time, affecting a region a few micrometers wide on either side of the boundary. However, within about 10 μm of the boundary, the Pd signal appears to have fully recovered. Grain boundary depletion has not been observed for the other boundaries but appears to represent the loss of Pd from grain 1, perhaps due to particularly favorable diffusion along this grain boundary or into the substrate bulk in

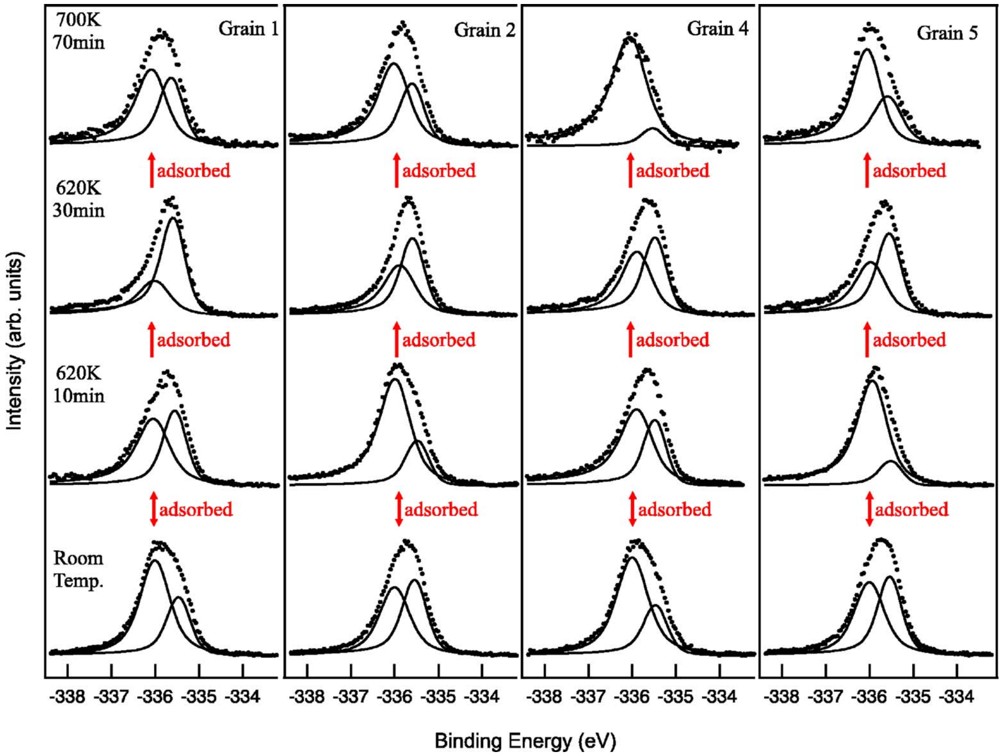

FIG. 4. (Color online) Small-spot Pd $3d_{5/2}$ photoemission spectra ($h\nu$=500 eV) for different grains, and for different temperatures and anneal times, showing the deconvolution into two components, $\mathrm{Pd}_{\mathrm{ads}}$ at 336.0±0.1 eV, and $\mathrm{Pd}_{\mathrm{alloy}}$ at 335.5±0.1 eV. The adsorbed components are indicated by the vertical arrows.

this region. It has been shown[3,5] that below 600 K diffusion is largely restricted to surface diffusion, but that above this temperature diffusion of Pd into the bulk becomes increasingly rapid.

In the SPEM study of Pd on Ni at room temperature,[1] it was shown that the Pd $3d$ photoelectron spectrum could be interpreted in terms of two forms of Pd, the proportions of which depended upon the grain being observed. The photoelectron spectrum was interpreted in terms of a high-binding-energy component associated with the presence of adsorbed Pd and a slightly lower-energy species associated with the formation of a surface PdNi alloy. Spectra of the Pd $3d$ shell deconvolved into their high- and low-binding-energy components, recorded at room temperature and for various annealing times at 620 and 700 K for grains 1, 2, 4, and 5 are shown in Fig. 4. All the spectra have been normalized to the same height for a better comparison. Good fits were obtained using Doniach-Sunjic functions[10] convolved with Gaussians to include instrumental broadening and other minor effects. Doniach-Sunjic functions are of the form

$$\frac{\Gamma(1-\alpha)}{[(E-E_L)^2+(\gamma_L^2/4)]^{(1-\alpha)/2}} \times\cos\left[\left(\frac{\pi\alpha}{2}\right)+(1-\alpha)\tan^{-1}\left(\frac{2(E-E_L)}{\gamma_L}\right)\right],$$

where Γ denotes the gamma function, E_L is the center energy, and γ_L the full width at half-maximum (FWHM) of a Lorentzian line shape. The term α represents an asymmetry present in core-level emission from metals that skews the line shape towards the higher-binding-energy half of the core line. The asymmetry parameter for the Doniach-Sunjic functions was 0.1 for both components of the Pd $3d$ spectra, the Lorentzian FWHM was 0.2 eV for the low-binding-energy component, and 0.5 eV for the high-binding-energy component. The Gaussian FWHM was fixed at 0.5 eV. The binding energies were found to be consistent with the room-temperature values (335.5 and 336.0 eV, respectively), to within ±0.1 eV.

The ratio of the two components used to fit the Pd $3d$ spectra at room temperature changes significantly on annealing. At room temperature, grains 1 and 4 both show that the adsorbed form of Pd is dominant, while for grains 2 and 5 the concentrations of adsorbed Pd and alloyed Pd are broadly similar. At 620 K, the proportions of adsorbed and alloyed Pd appear to depend upon annealing time. For grains 1 and 4 the alloy feature has increased after 10 min and continues to increase, becoming the dominant feature after 30 min after which no further change is observed. For grains 2 and 5 a more complicated behavior is observed. After 10 min annealing, the adsorbed feature has become the dominant component of the Pd $3d$ peak, but this trend is reversed after the sample has been subjected to a further 20 min anneal, with the alloyed feature then becoming dominant. It is significant that, within the probable accuracy of the deconvolution procedure, spectra from all grains show similar ratios after a total of 30 min annealing, and this is not changed by further annealing. All the spectra taken after annealing at 700 K appear broadly similar from the deconvolution analysis, with annealing time playing no obvious part in the nature of the surface Pd, but the spectra are significantly different from those produced by the 620 K anneal. Here the high-energy adsorbed-Pd feature has become dominant for all the grains.

The evolution of a thin Pd film (0.07 ML) on a Ni(110) single crystal has also been studied by means of STM.[5] After annealing at 520 K for 15 min the formation of rounded, 1-ML-high islands near or attached to the steps was observed. In the same work, the deposition of a thicker Pd film (3 ML) was also studied. In this case, the same annealing led to the formation of an ordered Pd adlayer totally covering the underlying Ni substrate.

For the experimental setup used here, the detected photoemission intensity of Pd and Ni is not expected to be sensitive to local Pd redistribution such as the formation of monolayer-high clusters within a given grain. Changes in intensity of the magnitude observed in Fig. 1 can only be a result of changes in Pd concentration between the various surface grains. As discussed previously,[1] the contrast in the room-temperature study can be interpreted in terms of initial mobility of the Pd atoms and differences in the ability of the various grains to accommodate Pd atoms. Incident Pd atoms, randomly distributed, have enough thermal energy to redistribute over the polycrystalline surface and adhere to the most favourable sites. The component of the Pd 3*d* photoelectron spectrum observed at a binding energy of 335.5 eV is believed to correspond to the formation of a surface Pd/Ni alloy, while that at 336.0 eV corresponds to simple Pd adsorption. The proportion of $\mathrm{Pd}_{\mathrm{ads}}$ to $\mathrm{Pd}_{\mathrm{alloy}}$ for a particular spectrum depended upon the nature of the surface grain on which it was absorbed. Similar components in the Pd 3*d* XPS spectrum (Mg K_α) have been interpreted in terms of bulk and surface components of an alloy-shifted core level.[4,7] However, the lower kinetic energy ($\approx$160 eV) and grazing emission angle (20° to the sample surface) used in that work should have lead to enhanced surface sensitivity.[11]

The changes in the contrast of the images occurring on annealing seem to be associated with the surface mobility of Pd atoms, but the fact that annealing at 700 K produces a different outcome from extended annealing at 620 K suggests there is an activation threshold that inhibits the onset of some processes, and thus the existence of kinetic barriers that are crossed between the two temperatures used for this experiment. The fact that the Pd/Ni ratio image does not change significantly with the annealing time suggests that any activated surface processes occur within the first few minutes of annealing. The large differences in the deconvolved spectra from the Pd 3*d* photopeaks after annealing at different temperatures strongly suggest that we are looking simply at surface effects.

IV. CONCLUSION

The present results show the complexity of the processes occurring during annealing of thin metal films deposited on polycrystalline substrates. In the particular Pd/Ni system studied, Pd atoms distributed inhomogeneously after room-temperature deposition undergo further reorganizations, involving alloying, de-alloying and bulk penetration. As discussed in our previous room-temperature study,[1] the contrast in the Pd/Ni ratio images can be interpreted in terms of the thermal energy required for Pd atoms to redistribute over the polycrystalline surface, and the capacity of the various grains to accommodate them. Figures 2 and 4 reveal that the annealing at 620 K affects both the local Pd surface concentration and the fraction of alloyed Pd atoms, the changes being different for the different grains.

Our previous μ-LEED measurements[1] on the sample used here suggest that grain 1 corresponded to a (100) Ni surface, grain 2 to a (110) surface, and grain 5 to a (111) surface. Poorly defined patterns from grains 3 and 4 suggest that these possess irregular or rough surfaces. According to the deconvolved spectra in Fig. 4, alloying is most efficient on the (100) grain, where the component corresponding to alloyed Pd becomes more pronounced with increasing annealing time. The reason for the significant decrease in the amount of alloyed Pd after annealing at 700 K is not clear. Grains 1, 2, and 5, which have a definite long-range order, show a small increase in the Pd/Ni ratio (10%–20%) after the 700 K annealing, which is compatible with the partial de-alloying evidenced by the spectra. The changes in the Pd/Ni intensity ratios shown in Figs. 1 and 2 indicate variations in the Pd concentration between the surface grains, which can also be attributed to penetration of Pd below the surface. The penetration seems to occur on grain 1, where the alloying is most pronounced, and on grain 4, which can be considered a rough surface, as LEED measurements indicate no long-range structural order. Another process that occurs is the depletion of Pd at the grain boundaries and on the rough surface of grain 4 (see Fig. 2 and the Pd/Ni intensity ratio profiles in Fig. 3), which can be attributed to the lower barrier for bulk penetration in these highly defective regions of the surface.

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