Formation and Decomposition of Palladium Hydride Particles

IMAGING PICTURES ON THE NANOMETRE SCALE

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Nanoscale changes in surface structure that accompany the low temperature exposure of palladium to hydrogen are reported. Field Emission Microscopy, a method for rapid in situ imaging of surface processes, has been used to examine palladium tips of radius ~ 200 nm, produced by a novel technique. Images are presented of the initial stages of the uptake of hydrogen. Subsurface hydrides were initially formed when palladium tips were exposed to hydrogen gas at low temperatures, starting at highly open surfaces present on the tip. Extruding PdH particles were also formed on top of the palladium tip and their growth was observed to proceed in a 'staccato'-like manner. Palladium crystallites remained on the surface after most of the hydrogen had been removed from the palladium sample by heating in vacuum. On heating the crystallites remained quite stable up to a temperature of ~ 700 K, but then melted back into the tip.

A detailed understanding of the process of hydrogen absorption by metallic phases (metals, alloys and intermetallic compounds) is important for the development of new materials for hydrogen storage. The interaction of hydrogen with palladium in particular has been extensively studied (1, 2), since the first report of the absorption of hydrogen into palladium in 1866 and since the first measurements of the palladium-hydrogen pressure-constitution-temperature relationship in 1895 (3). Two non-stoichiometric hydride phases can co-exist below the critical temperature (~ 300°C), and on going from the α- to the β-phase there are large increases in volume, with the lattice constant increasing by ~ 3.3 per cent, which is a volume increase of ~ 11 per cent. These changes occur continuously over the phase transition.

It is surprising that comparatively few studies have been focused on the structural changes occurring at the metal surface under the strain of the expanding lattice. Triangular shapes, of ~ 10 to 20 μm in size, have been seen developing during the early stages of hydrogen loading of a Pd(111) single crystal (4). In addition, networks in parallel lines have been observed on large single crystals by Sugeno and Kawabe (5). These patterns became apparent on complete transformation to the β-phase and could sometimes be seen after desorption of hydrogen (5).

Field Emission Microscopy (FEM) (resolution ~ 2 nm) images of surface processes were observed *in situ* during exposure of stable clean palladium tips to hydrogen, see Figure 1. The tips, produced by a novel technique (6), were held in hydrogen at a pressure of 2.6×10^{-4} mbar and 147 K. Figure 1(a) is characteristic of a clean palladium tip with the (110) plane in its centre. In general, a FEM pattern represents a work function map of the various crystal faces on the end of a hemispherically shaped single crystal tip. Figure 1(b) shows the growth of high intensity patches (that is, patches of increased
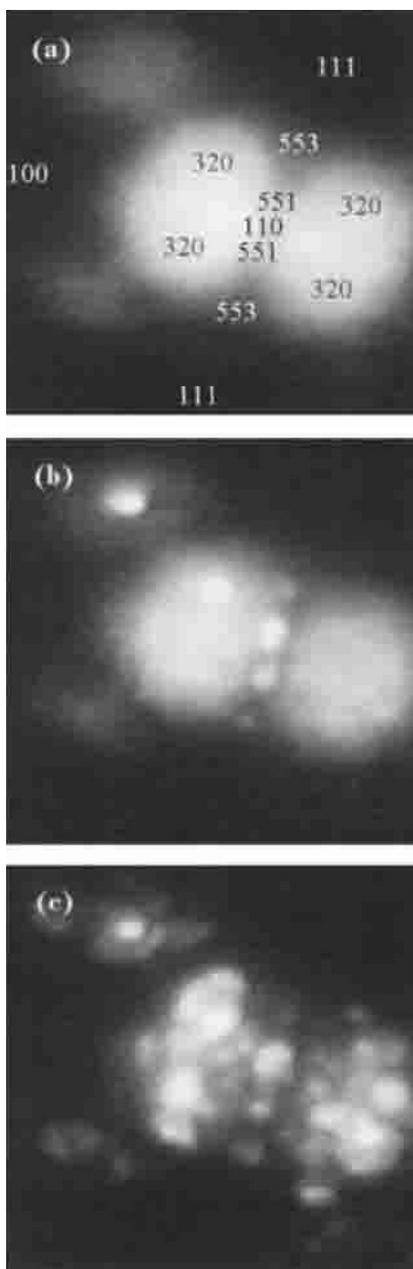
Fig. 1 (a) A clean palladium tip, produced by a new technique for making atomic tips for Field Emission Microscopy, showing the disposition of the principal faces.
(b) After dosing with hydrogen at a rate of 1040×10^{-6} mbar s, at 147 K, showing the initial build-up of high emission centres on the more open surfaces.
(c) After dosing with hydrogen at 26×10^{-3} mbar s, and 147 K, showing the situation at saturation

case at saturation is represented, where these high intensity patches stop growing.

Surfaces defects have been found to be very important for the low temperature uptake of hydrogen below 147 K (7, 8). At 147 K, no build-up of such high electron emission centres has been observed at pressures below the one primarily studied here.

We have examined in detail the 'staccato'-like growth of these novel structures. There appears to be overall continuous slow growth of particles, separated by periods of acceleration. The shape of most of the particles was rectangular or triangular, with the latter having previously been seen on a larger scale on the Pd(111) surface (4). After evacuation of hydrogen from the gas phase, such structures formed on the surface at 147 K still remained intact.

The effects of heating the hydrided tip are shown in Figure 2. The majority of the hydrogen desorbs from the tip at ~190 K, but many of the structures formed have remained on the surface (6). There are only slight changes in the palladium tip between 300 K (Figure 2(a)) and 600 K (Figure 2(b)), with Figure 2(b) showing the situation after several minutes at 600 K. For the low-temperature H_2-loaded palladium wire and for a Pd(110) surface, no high temperature β-desorption peak has been observed, suggesting that there was no hydrogen penetration into the bulk (9–11). However, the β-desorption peak does appear when hydrogen is loaded at a temperature of 300 K. With the palladium wire, heated at a rate of 5 K s⁻¹, the β-peak appears at 620 K (11).

Even if hydrogen had still been present in the palladium tip, it would have diffused out of the sample after several minutes at 600 K (7–11). It therefore seems possible to conclude that the patches left on the surface at this point are palladium microcrystals, still on top of the palladium tip. At 700 K however (Figure 2(c)) these crystallites have all but disappeared, the obvious interpretation being that the palladium atoms

work function) first occurring around (551) surfaces, which are basically (110) terraces separated by (111) steps. Similar structures were found to grow on a very open (320) face, and were also observed on the (553) surfaces. In Figure 1(c) the

Fig. 2 FEM image of a palladium tip in vacuum after low temperature hydrogen loading:
(a) At 300 K, where the bulk of hydrogen has been removed, but the structures formed on the surface remain.
(b) At 600 K, where any remaining hydrogen will have desorbed, and only palladium microcrystallites remain on top of the palladium tip.
(c) At 700 K, at which point palladium atoms have become mobile, so that the palladium microcrystallites dissolve back into the tip


are now becoming mobile and that the palladium microcrystals are melting back into the tip.

One of the questions that remains to be answered is whether the structures formed on the palladium surface under the hydrogen dosing at low temperature (that is, 147 K), also contain hydrogen, or whether they are pure palladium crystals formed on top of a surface hydride. It is clear that the palladium atoms are mobile on the surface at low temperatures under the influence of an expanding PdH lattice, although possibly only in the topmost layers of the tip.

The staccato growth of the treated particles gives an indication that the structures are actually PdH crystallites at low temperature. The slow growth can be equated to PdH lattice expansions in α- to β-phase transitions and the accelerated growth periods can be equated to stress causing palladium atoms to radically change positions. Indeed, the fact that the tip could take on a new orientation after high temperature annealing of a sample exposed to H_2 at low temperatures, also seems to indicate the influence of stress.

Conclusions

The use of FEM has provided a high resolution view of the kinetics of the initial stages of PdH formation at palladium surfaces exposed to H_2 at low temperatures. At patches of increased emission, initiated on the more open surfaces of the palladium tip, growth is mainly slow – since the palladium lattice must expand in taking up the hydrogen atoms, but there are rapid increases in the growth rate as the strains in the β-phase cause atoms to be expelled or rearranged. At saturation the particles have grown not only two dimensionally, but also in height, such that when hydrogen is removed, microcrystals of palladium remain on top of the palladium tip. These palladium microcrystals are stable until temperatures are reached at which the palladium atoms become thermally activated. The fact
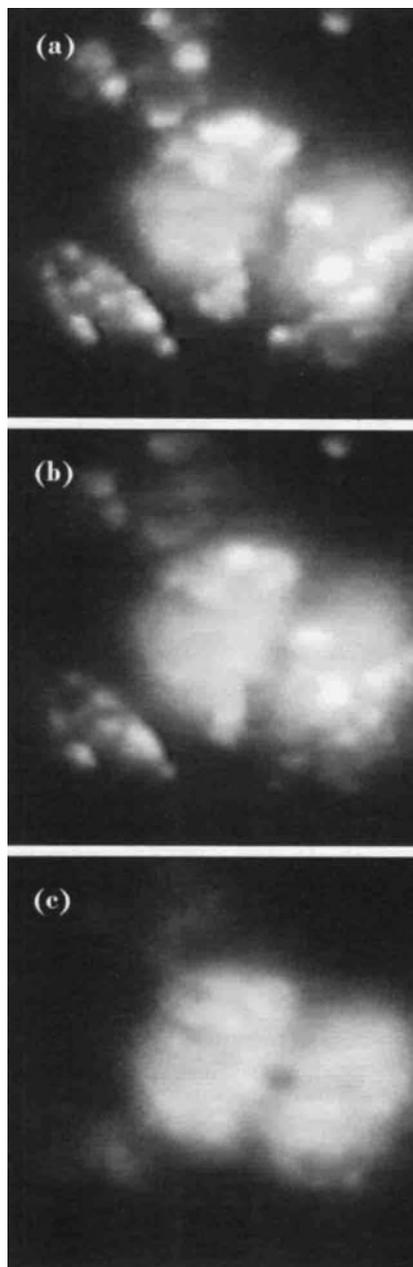
that hydrogen has the ability to cause movement of the palladium atoms at such low temperatures is significant. Indeed, many recent studies have shown that such metal surfaces can be quite mobile and the present study has demonstrated that

large reconstructions can occur when palladium interacts with hydrogen at 150 K. However, in the bulk of a metal in which a hydride is being formed, there are few places for the atoms to go when the lattice expands. As a consequence it would appear that more thought needs to be given to stabilising the surface in order to prevent material degradation, when metal-hydrogen reservoirs are being designed.
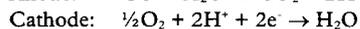
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Carbon Monoxide Sensing Technology

Growing awareness of the hazard of carbon monoxide (CO) in the home environment has aroused great interest in detector alarms in the U.K. and North America. Various sensing technologies have been used to detect the gas.

The first commercial sensor, the Taguchi sensor, correlated the change in conductivity of a heated tin oxide pellet to the concentration of CO present. However, due to its high power requirements, this sensor required mains wiring. The first battery powered CO detectors used an optical detection technique based on colour chemistry, the colour change being the same as in the formation of carboxyhaemoglobin in the blood.

Recently, electrochemical units, suitable for use in battery powered alarms, have become commercially available. These have significant advantages over prior technologies in their accuracy and reliability over a wide range of gas concentrations. Some instruments have visual displays to differentiate between acute high CO concentrations and hazardous chronic low concentrations. Carbon monoxide and oxygen diffuse into the sensor from the ambient air to react:

Anode: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$
Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Overall: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

The current flowing between the anode and cathode through an external circuit is proportional to the CO present over a wide concentration range. The carbon dioxide (CO_2) that is produced diffuses out from the sensor.

The electrode reactions take place under acidic conditions to avoid a build up of CO_2 in the sensor. Under these conditions platinum is required to catalyse the electrode reactions. Platinum has the ability to form a range of chemisorbed surface species, thereby lowering the activation energy of intermolecular reactions. Platinum forms carbonyl species and surface bound hydroxyl species required for the overall anode reaction.

In practice porous electrodes made from a high surface area platinum material are used. This provides a three-phase boundary between the gas, the electrolyte and the electrode where the electrode reactions can occur rapidly in the presence of CO.   GAVIN TROUGHTON

Platinum Labware Catalog

Alfa Aesar in North America has just published a "Platinum Labware Catalog" which describes a range of laboratory products incorporating platinum, platinum group metals and Zirconia Grain Stabilised (ZGS) platinum, utilising the inertness and malleability of platinum.

The catalogue describes typical uses of the equipment and contains reference data and information on a recycling programme.

To obtain a copy of the catalog contact Alfa Aesar; in North America, tel: 800-343-0660 ext. 6404, fax: 800-322-4757; Rest of the World, tel: 978-521-6404, fax: 978-521-6350.