

Atomic-resolution scanning tunneling microscopy of a palladium surface

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A palladium surface has been studied at atomic resolution by scanning tunneling microscopy in a controlled gaseous atmosphere. A comparative analysis was made of the surface of a palladium sample which was subjected to sequential heat treatment in atmospheres of oxygen and hydrogen and the surface of untreated palladium.

Palladium alloys which are selectively permeable to H_2 are used as membrane catalysts in reactions involving hydrogen and are also widely used for purifying hydrogen.¹ The activity and selectivity of these catalysts depend strongly on the concentration of hydrogen dissolved in them, so it is worthwhile to study the absorption of hydrogen by palladium and its alloys.

The hydrogen–palladium state diagram has a region of a solid solution of hydrogen in palladium, with a concentration ratio $n_H/n_{Pd}=0.02$ (this is the α phase), and it also has a β phase, in which the concentration ratio varies from $n_H/n_{Pd}=0.6$ to complete saturation, palladium hydride (PdH). A comparative series of isothermal characteristics was given in Ref. 2. According to the data of Ref. 3, the lattice constants of palladium and its alloys change only negligibly upon the sorption of hydrogen. For the less-hydrogen-saturated α phase of palladium, the lattice constant is 3.89 Å, while for the more-hydrogen-saturated β phase it is 4.04 Å.

In this letter we are reporting a study of the surface topography of polycrystalline palladium (with a purity > 99.99%) by scanning tunneling microscopy (STM) in an atmosphere of oxygen and hydrogen. Measurements were carried out both under ordinary atmospheric conditions and after an annealing-reduction cycle in gaseous O_2 and H_2 . The probe tip was fabricated from platinum–iridium wire.

In the experiments, the system was first evacuated to $p \sim 10^{-2}$ torr, and then oxygen was admitted into the vacuum chamber to a pressure of 10 torr. The polycrystalline palladium sample was annealed in oxygen at 300 °C for 10 min. After cooling, the system was reevacuated to 10^{-2} torr, and then hydrogen was admitted to a pressure of 200 torr. At this amount of hydrogen, the palladium sample should be in the β phase at room temperature.² A subsequent annealing of the sample was carried out for 3 min at ~ 400 °C. After cooling, the hydrogen was pumped off, and the system was ready for the microscopy. The particular working conditions for the study of the surfaces of the palladium samples were selected in the course of the experiments. The optimum conditions were found to be a tunneling voltage $U_t = -0.02$ V, a tunneling current $I_t = 0.5$ nA, and a scanning velocity $V = 0.9$ Å/ms.

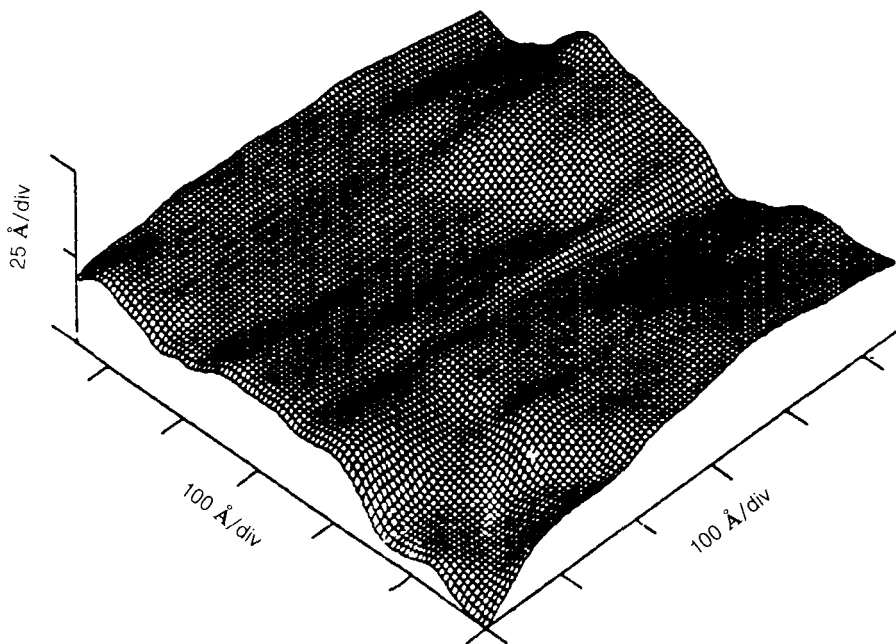


FIG. 1. Image of the surface of a palladium sample which has undergone sequential heat treatment in oxygen and hydrogen.

The surface of the palladium sample was first measured under ordinary atmospheric conditions at scales from 500 to 3000 Å. Irregularities with typical sizes of 300–500 Å in the plane of the sample and on the order of 50 Å high were found on the surface. Figure 1 shows an image of a sample which was treated in oxidizing and reducing media beforehand, by the procedure described above. A side of this frame corresponds to 570 Å. In addition to the irregularities which we just mentioned, this image reveals that many new irregularities, much smaller in size (with an average diameter ~ 100 Å and a height ~ 15 Å), appear on the surface. The results agree well with the data of Ref. 4, where palladium was saturated with hydrogen by an electrochemical technique. The results can be described by the following simple model.

We assume that after the palladium interacts with the hydrogen some irregularities with the shape of a spherical segment arise on the palladium surface. The unit cell of palladium in the β phase is known to be 4.04 Å, while that for pure palladium is 3.89 Å. We assume that the area of the base of the spherical segment represents the palladium surface before the interaction with the hydrogen. We then conclude that there are 520 unit cells over an area of 7850 \AA^2 (this figure corresponds to an average diameter of about 100 Å). The same number of cells, but with a lattice constant 4.04 Å, must fit onto the spherical surface of the spherical segment, which we take to be the surface of the sample after the interaction with hydrogen. A simple calculation shows that the height of the spherical segment must then be 15–20 Å. This figure agrees well

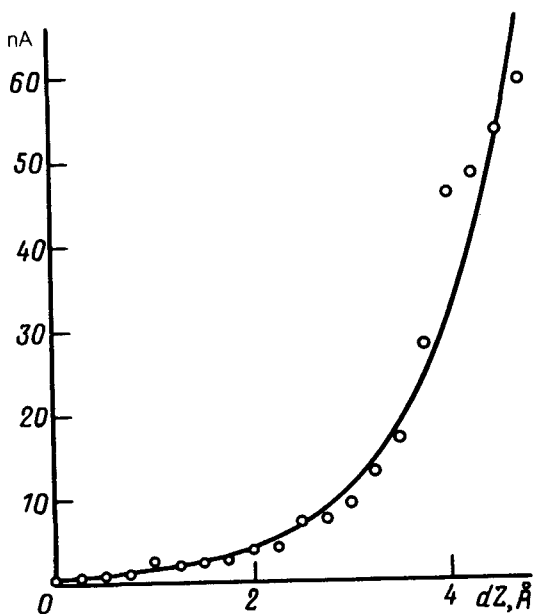


FIG. 2. Tunneling current versus the gap size.

with the results found experimentally. This estimate may prove completely satisfactory for describing irregularities of macroscopic size.

To determine the local height of the barrier on a sample of polycrystalline palladium in the β phase, we measured the tunneling current as a function of the gap size. Figure 2 shows a typical result. The local barrier height can be estimated from $I \sim A \exp(-\varphi^{1/2}z)$, $I_1 I_2 = \exp[-\varphi^{1/2}(z_1 - z_2)] = 1/100$. It follows that we have $\varphi \sim 1$ eV (for a clean palladium surface we would have $\varphi \sim 4.8$ eV). For graphite in air, the value $\varphi \sim 1/25$ eV has been found, while for gold films the value is⁵ $\varphi < 1$ eV. The decrease in the local height of the barrier in all these examples may occur because the tip makes contact with the surface as a result of the presence of contaminants or an adsorbed film on the surface.⁶ It can thus be concluded that an adsorbed layer on the surface of a palladium sample decreases in size after the sample has been subjected to sequential heat treatment in oxygen and hydrogen.

An atomic resolution was achieved by the following technique. A preliminary observation was carried out at a large scale (about 500 \AA). A region $300 \times 300 \text{ \AA}$ in size was selected on the surface. A voltage of about 10 V was then applied between the sample and the tip (the feedback circuit was open in this step). The size of the scanning field was then reduced to a few tens of angstroms. The apparent reason for the achievement of atomic resolution under these conditions is that the electric field causes a change in the adsorbed layer on the palladium surface. According to mass



FIG. 3. Crystal lattice of palladium (X : 42.6 Å. Y : 40.8 Å. Z : 0.7 Å).

spectrometry, this layer consists mostly of oxygen and hydrogen. The same conclusion is implied by the fact that the crystal structure of palladium can be observed for 5–6 min after it has “swollen.” The measured lattice constant (Fig. 3) is 4.0 ± 0.2 Å; this is approximately the lattice constant of the crystal lattice of palladium. The measurement error is 0.2 Å, so it would be incorrect to say that the value found here is the lattice constant of palladium in specifically the β phase. The height of the atomic corrugation which results is 0.7 ± 0.2 Å. When this technique is used for a palladium sample which has not been subjected to heat treatment in oxygen and hydrogen, the desired results are not achieved.

In summary, a palladium surface has been studied at atomic resolution by STM in a method involving a sequential annealing of the sample in oxygen and hydrogen. The measured lattice constant of palladium in the β phase is 4.0 ± 0.2 Å, in good agreement with theoretical results and also with the results reported in Ref. 3. The surface topography of a palladium sample which has been subjected to sequential heat treatment in oxygen and hydrogen has been compared with that of a sample prepared under ordinary atmospheric conditions.

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