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Ex Situ Observation of Electrochemically Hydrogenated Palladium Using a Scanning Tunneling Microscope

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Morphological transformations were observed *ex situ* on a palladium (Pd) surface induced by electrochemically absorbed hydrogen using a scanning tunneling microscope (STM). Hydrogenated Pd exhibited β-phase and hydrogen absorption into Pd transformed the surface into a more detailed, nodular-like structure.

The absorption of hydrogen by Pd is an attractive phenomenon because it is utilized in hydrogen storage and battery industrial applications,[1] and also because hydrogen-rich Pd shows the possibility of superconductivity. Additionally, much attention has recently focused on the process of deuterium absorption into a Pd electrode, i.e., so-called cold nuclear fusion.[2-4] The Pd/H_2 absorption mechanism has been extensively investigated, yet only a few reports concerning its geometrical and structural properties have been published,[5] thus leading to the use of the scanning tunneling microscope (STM) to electrochemically study hydrogen absorption into a Pd electrode in order to provide nanometer scale insights into the structural properties of conductive solid surfaces.

Electrochemical hydrogen absorption into a Pd (polycrystalline, 99.95%) electrode was galvanostatically conducted for three hours in 1.5 mol dm^{-3} H_2SO_4 aqueous solution[6] with a constant cathodic current density of 500 mA cm^{-2}.

Figure 1 shows X-ray diffraction patterns of the Pd sample before electrolysis (blank sample) and after electrolysis (Pd-H sample). The blank sample had a face-centered cubic (f.c.c.) lattice constant of 3.88-3.89 Å, in good agreement with the literature value,[7,8] however, the electrochemically treated Pd-H exhibited new peaks with a f.c.c. lattice constant of 4.02-4.03 Å. This is direct evidence that the blank sample was transformed by electrolysis into a β-phase Pd-H compound.

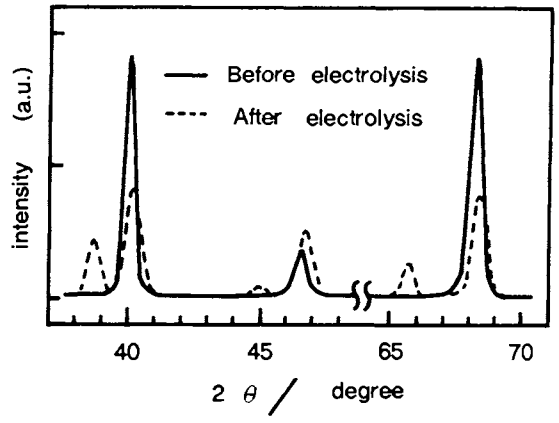

Fig.1. Palladium X-ray diffraction patterns.
Blank sample (before electrolysis).
Pd-H sample (after electrolysis).

The STM observation was performed in air at room temperature using a Nanoscope II microscope. Figures 2(a) and 2(b) respectively show macroscopic STM images of the blank and Pd-H samples. Many vertical lines and several corrugations can be clearly seen on the blank sample surface, and after electrolysis the line spacing between them expanded and the corrugations swelled.

Typical STM images of the blank and Pd-H samples are respectively shown in Figs. 3(a) and 3(b). It is clearly evident that the Pd-H sample surface has a more detailed and refined structure than the blank sample surface. This change is believed to be the result of regions which are separated by lattice defects, e.g. grain boundaries, becoming morphologically transformed into a more distinctly perceptible surface due to the absorption of hydrogen into Pd and the formation of a Pd-H compound.

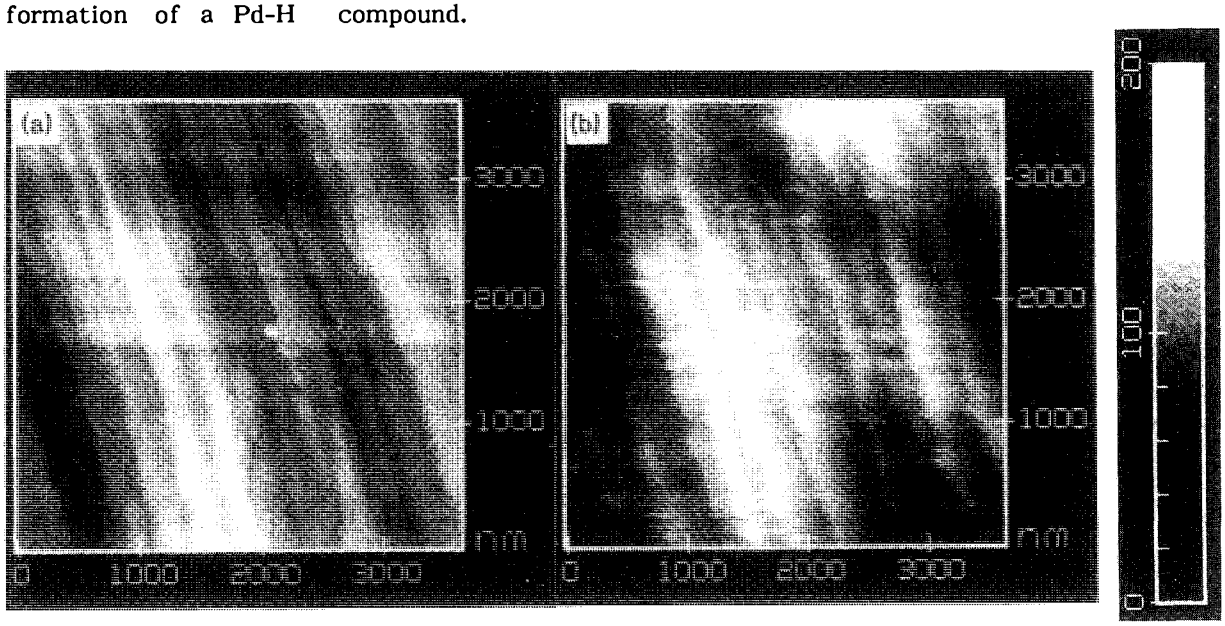

Fig.2. Palladium surface STM images.
(a) Blank sample, (b) Pd-H sample, scan area : 3600 nm, sample bias : -20.1 mV, tunneling current : 5 nA.

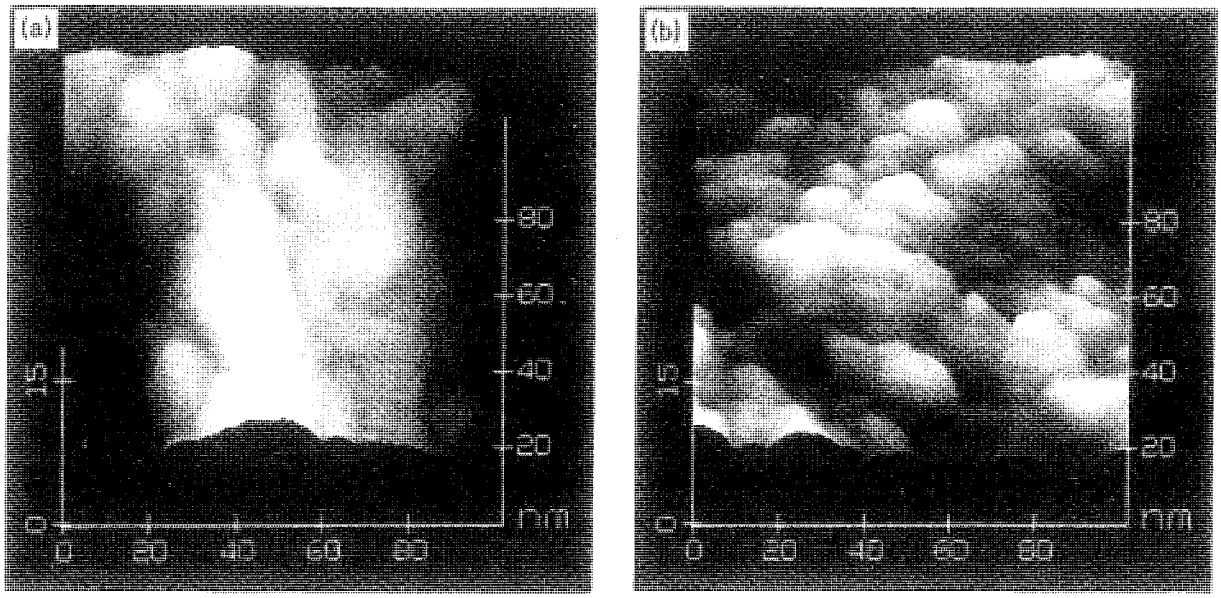

Fig.3. Palladium surface STM images.
(a) Blank sample, (b) Pd-H sample, scan area : 100 nm, sample bias : -20.1 mV, tunneling current : 5 nA.

A schematical illustration of this process is presented in Fig. 4. Domains of the blank sample surface contain lattice defects (Fig. 4(a)), although they are difficult to see in an STM image (Fig. 3(a)). Hydrogen ions are adsorbed and are reduced on the surface, with some of them permeating into the Pd bulk. These permeated hydrogens then accumulate in the regions separated by the lattice defects. The regions have individually, morphologically grown into a Pd-H phase as a result of hydrogen absorption (Fig. 4(b)), and finally, the surface is transformed into a more detailed, nodular-like structure (Fig. 4(c)).

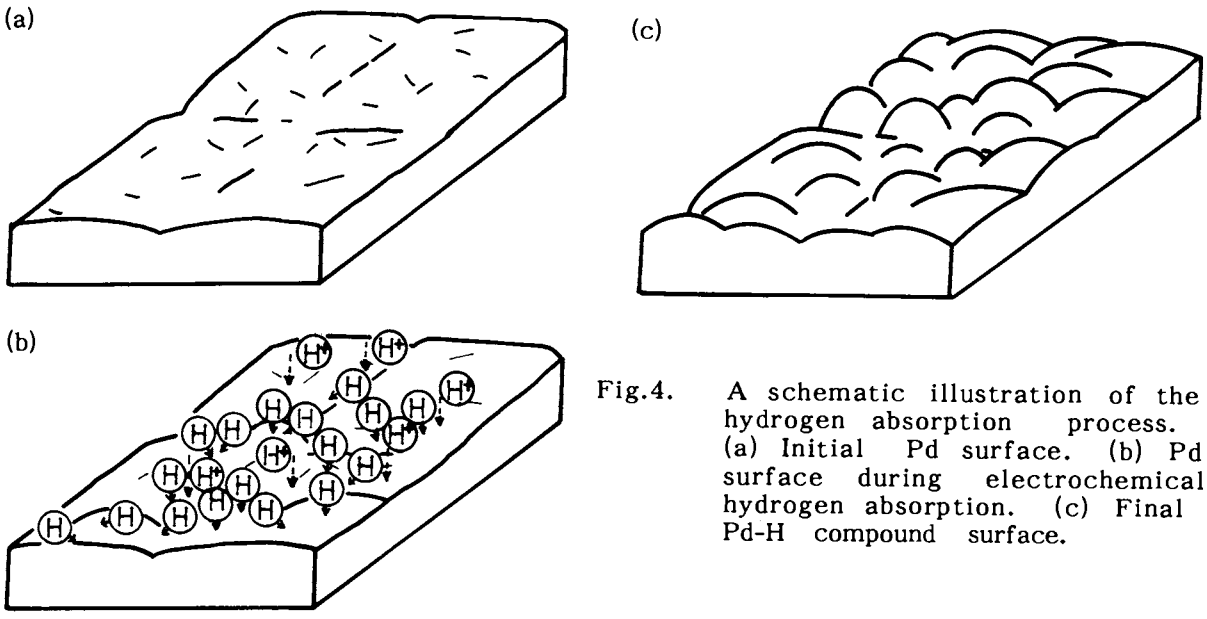

Fig.4. A schematic illustration of the hydrogen absorption process. (a) Initial Pd surface. (b) Pd surface during electrochemical hydrogen absorption. (c) Final Pd-H compound surface.

Here we have to think over the hydrogen evolution and the reaction of hydrogen with oxygen. Those reactions in a scanning area may cause the instability at STM tunnel junction. Actually, the measurement was sometimes difficult under the present conditions. This is probably because the STM tip was set just on those reaction areas. However, in Fig. 2(b), showing a macroscopic image of the Pd-H surface, the site morphologically influenced by those reactions was not observed. Instead of that, the image that the Pd surface swelled by hydrogen absorption was observed. The scanning area shown in Fig. 3(b) is the same as that shown in Fig. 2(b). Therefore it is reasonably assumed that neither the hydrogen evolution nor the reaction of hydrogen with oxygen did not affect the STM image shown in Fig. 3(b). Moreover, the image shown in Fig. 3(b) is a typical microscopic one in all of the images observed on the Pd-H sample surface in our experiment. Those STM images were observed in air. If Pd-H sample was set in vacuum, the desorption of hydrogen has to be considered. That is the case with, for example, SEM measurement. Therefore STM is an advantageous method to observe the surface of a Pd-H.

In conclusion, the STM was used to investigate *ex situ* morphological transformation of a Pd surface by hydrogen absorption. The Pd surface swelled, the lattice constant increased, and hydrogen absorption into the Pd transformed the surface into a more detailed , nodular-like structure. Further studies are presently in progress.

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