Hydrogen absorption in palladium films sensed by changes in their resistivity

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Received 1 November 1996; accepted 7 February 1997

The resistance of pure palladium films of 11, 30 and 54 nm thickness was monitored during their exposure to H_2 at pressures ranging between 1 and 20 Torr. After completing a cycle of H_2 absorption/desorption, the resistivity changed in a "saw tooth" fashion similar to the changes observed in surface adsorption of hydrogen by other transition metals. Large resistance changes are observed in these studies, confirming that bulk hydrogen absorption occurs in Pd while hydrogen surface adsorption becomes dominant over bulk absorption in other metals such as niobium. The resistance change curves carry the information of the kinetics of absorption.

Keywords: hydrogen absorption, palladium films, hydrogen diffusion, resistance measurements, electron microscopy, electron diffraction

1. Introduction

The process of hydrogen absorption–desorption by transition metals is an important issue in catalysis and hydrogen storage. Palladium and palladium alloys play an important role in these research areas since Pd has unique diffusion properties for hydrogen. For instance, Pd membranes are used in a variety of hydrocarbon catalytic processes, hydrogen purification, and hydrogen production from the reaction of methanol and water [1]. Many details of the basic mechanisms of hydrogen permeation through Pd are not clearly understood and membrane failures is still a problem [2].

The permeation of hydrogen through Pd is a multistep process which involves the following steps: (1) reversible dissociative chemisorption of H_2 by the Pd surface, (2) reversible dissolution of surface atomic H at Pd subsurface sites, and (3) diffusion of atomic H in bulk Pd. In a Pd membrane with a surface atomically clean, the permeation of hydrogen is limited by the dissolution of H atoms in subsurface sites. This is because the surface chemisorption of H_2 is not activated and occurs very fast [3,4].

We have measured the hydrogen desorption spectra (TDS) of Pd and Pd alloys [5–7], and found significant differences in the spectra between Pd and other metals which do not absorb hydrogen [8]. The desorption spectra of hydrogen from Pd imply bulk absorption, whereas in the case of the other metals the hydrogen is confined to the surface. TDS has been traditionally a technique used to study the kinetics of surface adsorption but we have demonstrated in our prior work [5–7] that it can also be used to determine absorption kinetics of the bulk material.

In the same way Shanabarger [9–11] studied the surface adsorption of hydrogen on thin Ni and Fe films from changes in their resistivities when they adsorb the gas. Pick et al. [12,13] and Strongin et al. [14] studied the absorption of hydrogen on Nb and Pd-capped Nb films also from resistivity measurements. Resistance change of the films when they absorb gases carries important information of adsorption kinetics.

It is plausible then to use this characterization technique to determine the hydrogen absorption kinetics by bulk Pd. Since the resistance change of bulk Pd due to hydrogen absorption is expected to be small, this effect would be more readily detectable in thin films of Pd.

The current accepted explanation why the resistance of the Ni or Nb film changes when H_2 (or gas in general) is adsorbed on their surfaces can be found in the description of the Fuchs–Sondheimer model [15]. This model hypothesizes that the surface adsorbed molecules increase the resistance of the film by increasing the diffusive scattering of specularly reflected conduction electrons from the gas–solid interface. This is assuming that the surface morphology of the film is perfectly planar. A refinement of this last model, "the scattering hypothesis" is a more general case of the Fuchs–Sondheimer model. In this model, surface roughness is considered and therefore adsorbed molecules only increase the fraction of scattering centers on the surface which cause diffused scattering of conduction electrons.

These scattering centers are proportional to the hydrogen surface coverage and thus it is expected that the curve of resistance change would carry kinetic information of the surface adsorption process. In a Pd film exposed to H_2, a larger resistance change than corre-

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sponding to surface adsorption is expected since Pd absorbs hydrogen in the bulk. In this case the scattering centers (hydrogen atoms dissolved in the bulk) will be located throughout the film and the resistance change of the film will not be only confined to the surface. The resistance change curve would carry kinetic information of the adsorption and/or diffusion of H in the film and this is what we had proposed to study in this work.

2. Experimental

Samples composed of 11, 30 or 54 nm palladium film evaporated onto a piece of mica of approximate dimensions of 1.0 × 1.0 × 0.01 cm were prepared in ultrahigh vacuum (UHV) and mounted on the manipulator of our testing system. Palladium ingots with a purity of 99.999%, obtained from Alfa Products, were used for the evaporation of the films. The flat piece of mica was painted at the ends of one face with a conductive paint (Loctite "Quick Grid", an emulsion of small metal particles in ethyl acetate). Once the paint had dried, the mica was masked with aluminum foil leaving an area of approximately 0.8 × 0.8 cm exposed where the Pd film was deposited. The films were evaporated with a background pressure in the low 10^{-8} Torr and the film thickness was measured with a quartz thickness monitor within 10% error.

Each side of the film where the conductive paint was placed, was spot-welded to a piece of insulated gold wire which was also spot-welded to a pin of a UHV feedthrough on the other end. The electrical feedthrough was connected to a Keithley MicroOhmmeter, model 580 to measure the resistance of the Pd film. More details of this system can be found elsewhere [16].

The Pd films were also characterized by transmission electron microscopy (TEM) using a Philips EM300 system [17]. Electron-transparent Pd films were obtained by thinning the mica substrate layer by layer until only the Pd films remained. Typically, Pd films of 500 Å were used for this characterization.

3. Results and discussion

Several Pd films were inspected with TEM. The films are smooth and free of bulk contamination. Typically, the morphology of the films appears composed of small crystals with a preferential orientation in the (1, 1, 1) direction. This preferential orientation was also observed in thin Pd foils [6,7]. An image of the film at a magnification of ×26 000 is displayed in figure 1. Two smooth gray areas corresponding to the Pd film can be seen in this photograph: a light gray area on top and a darker gray area at the bottom. The difference in gray color is due to the difference in thickness of the mica substrate, a lighter gray being a section of the sample more transparent to electrons. Two dark lines running almost parallel and diagonally in the lighter area of the Pd film can also be seen in the photograph: they correspond to grain boundaries which are separated by about 1 μm.

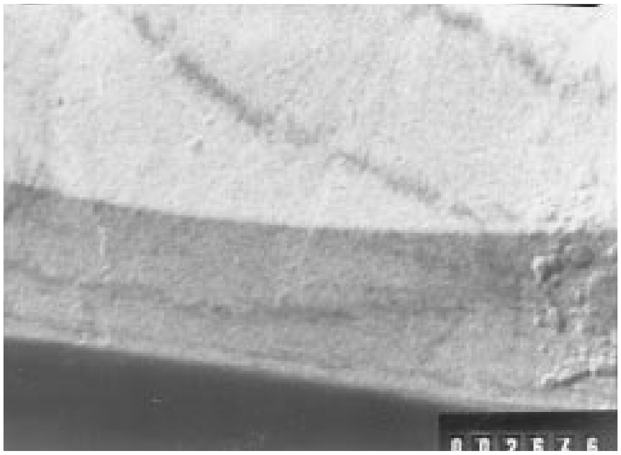

Figure 1. TEM image of 54 nm Pd film deposited on mica. The image was obtained ×26 000. The smooth light and dark gray areas correspond to the Pd film (the light area is more transparent to electrons due to thinner mica backing). Dark gray lines running almost parallel and diagonally in the light gray area correspond to grain boundaries.

The corresponding diffraction pattern is displayed in figure 2 . This diffraction pattern is composed of diffraction spots arranged in hexagonal pattern (which correspond to mica) and bright rings (which correspond to the Pd). Looking at the rings from the center outward, the first corresponds to the (1, 1, 1) direction (the brightest) and the other rings to the (2, 0, 0), (3, 2, 0) and (3, 1, 1) directions. From the radius of the circles (R_n), the corresponding wave-length of the electrons (λ) and a characteristic microscope distance sample/image (L), one can

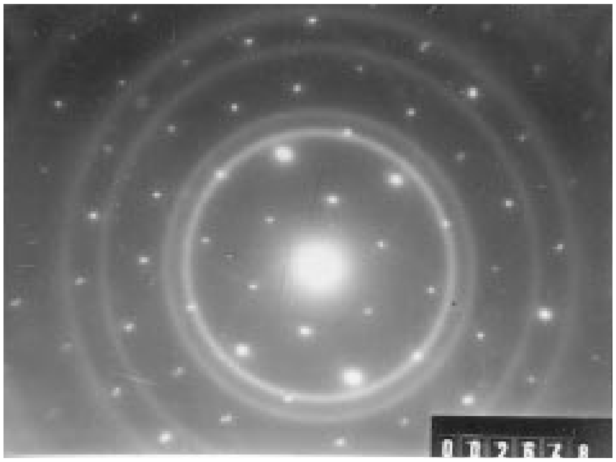

Figure 2. TEM electron diffraction pattern of the same area of the Pd film inspected in figure 1. Bright spots arranged in hexagonal pattern correspond to diffraction from mica and bright circles correspond to polycrystalline Pd. Absence of other diffraction lines indicates that the Pd film is free of bulk impurities.

calculate the lattice spacing $d_{h,k,l}$ according to the following formula:

$$\lambda L = R_n d_{h,k,l} \, . \tag{1}$$

Using $\lambda L = 3.94$ Å cm, which corresponds to our microscope set-up, we obtain a lattice constant equal to 3.83 Å, in good agreement with the lattice constant of bulk Pd (3.88 Å) [18].

A remarkable clean hexagonal diffraction pattern for mica can be seen in figure 2. This is not surprising since mica can be atomically smooth for distances as large as 1 cm^2 [19]. This property of mica makes it an ideal substrate for metallic films free of damage within those dimensions.

The Pd films were mounted onto the manipulator and introduced inside the controlled atmosphere chamber. Inside there, the samples were heated to 450 K in 700 Torr of H_2, as a cleaning procedure. The samples were then subjected to three cycles of heating in H_2 and in vacuum to remove all the hydrogen.

Assuming that no contaminants remained on the surface after the cleaning step, the sample at a temperature near 300 K was then exposed to a H_2 pressure ranging between 1 and 20 Torr. The resistivity change was measured and recorded during the H_2 exposure. For each pressure, the cleaning cycle was repeated before exposure to H_2.

The resistivity of the Pd film increased during exposure to H_2 and decreased to approximately the initial value when the H_2 was removed from the chamber. These changes were quite reproducible and a "sawtooth" pattern was obtained for a cycle of absorption/desorption for films of different thicknesses. This resistance change as a function of time is displayed in figure 3 for Pd films of 11, 30 and 54 nm exposed to H_2 pressures of 2.5, 2 and 4 Torr, respectively. We tried to perform the experiments at a constant film temperature near room temperature but this varied between 291 and 307 K.

The resistance change of the film exposed to H_2 can be fitted with an expression developed by Pick et al. [12]. Pick and coworkers performed careful experiments of H_2 adsorption in Nb films measuring the change of resistance of the films. Their analyses of the resistance change assumed some H dissolved in the bulk. The analytical expressions which fit the data are the following:

For resistance increase,

$$\tfrac{1}{2}(1-b)^2 \ln(1+y) - \tfrac{1}{2}(1+b)^2 \ln(1-y) - b^2 y = at \, , \tag{2}$$

where y is the normalized atomic fraction of H in the bulk ($y = x/x_{\max}$), t is time, and a and b are parameters obtained from the curve fit.

For resistance decrease,

$$2b \, \ln(y_0/y) + b^2(y_0 - y) + 1/y - 1/y_0 = at + c \, . \tag{3}$$

In this case, there are two more constants to fit, y_0 and c.

Pick et al. [12] related the constants a and b with physical parameters involved in the absorption process as follows:

$$b = \left(\frac{2\Gamma s_0}{N_s K} \right)^{1/2} \tag{4}$$

and

$$a = \frac{2\Gamma s_0}{N_s N_\ell x_{\max}} \, . \tag{5}$$

Γ is the flux of H_2 molecules at a given pressure, impinging 1 cm^2 of Pd surface per second; s_0 is the Pd sticking coefficient which in our case has a value near to 1 [1,4]; N_s is the number of Pd atoms per cm^2; N_ℓ is the number of Pd layers in the film; and K is the rate constant for absorption.

The rate constant follows an Arrhenius type of law:

$$K = K_0 \, e^{-2E/RT} \, , \tag{6}$$

where K_0 is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the temperature. The pre-exponential K_0 has a value around 10^{13} [12,13].

By combining eqs. (4), (5) and (6), the following relationship is obtained:

$$\ln(K_0) - 2E/RT = \ln(N_\ell a x_{\max}) - 2 \, \ln(b) \, . \tag{7}$$

The change in resistance (ΔR) is proportional to the atomic fraction x and this implies that the maximum change in resistance ($R_{\max}$) is also proportional to the maximum atomic fraction of H, $x_{\max}$. Bearing this in mind, typical data such as the one displayed in figure 3 can be directly fitted with eq. (2) for resistance increase and eq. (3) for resistance decrease. This was done for resistance increase and the fit is displayed as solid lines for the three curves shown in figure 3. In the three cases

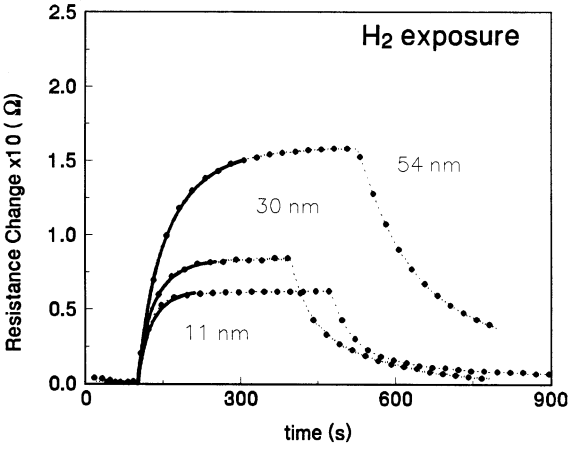

Figure 3. Resistance change of Pd films when exposed to different H_2 pressures: 11 nm thick at 2.5 Torr; 30 nm thick at 2 Torr; and 54 nm thick at 4 Torr.

$b = 1$ and a equal to 0.024 s^{-1} for 54 nm; 0.043 s^{-1} for 30 nm; and 0.056 s^{-1} for 11 nm.

From eq. (7), using these parameters a and b and our experimental conditions, the activation energy for absorption can be obtained. The resulting calculations yielded 8.9 kcal/mol for the absorption on the 54 nm Pd film and 8.8 kcal/mol for the 11 nm film, in excellent agreement with our thermal desorption measurements of hydrogen from Pd foils [5].

In our experiments, the resistance change of the Pd films at a constant temperature and H_2 pressure increases until it reaches a saturation value. We plotted (figure 4) the relative final resistance change as a function of the square root of the H_2 pressure for each Pd film studied. The data for the three Pd films start to deviate from the linear relationship at a value around 8.5 Torr. After this value, the relative resistance change remained constant independently of the hydrogen pressure.

According to the phase diagram obtained by Frieske and Wicke [20] these conditions correspond to the α phase of Pd hydrides. The equilibrium solubility isotherm of PdH_n obtained around 307 K and displayed in this phase diagram showed that n changes continuously from 0 to 0.15 as a function of the pressure up to about 7.5 Torr ($n = x_{max}$ for our case). The hydrogen concentration x_{max} continues to change from 0.15 to 0.6 if Pd is kept under these conditions (307 K and 7.5 Torr). Apparently this hydrogen absorption regime (between 0.15 and 0.6) is not sensed by the resistance change of the film.

The curves of the relative resistance change as a function of the square root of the H_2 pressure overlapped for all the Pd films and it has a linear dependence on $P^{1/2}$. A line obeying the following equation fits almost all the data in figure 4:

$$(\Delta R_{max}/R) \times 100 = 1.9P^{1/2} . \qquad (8)$$

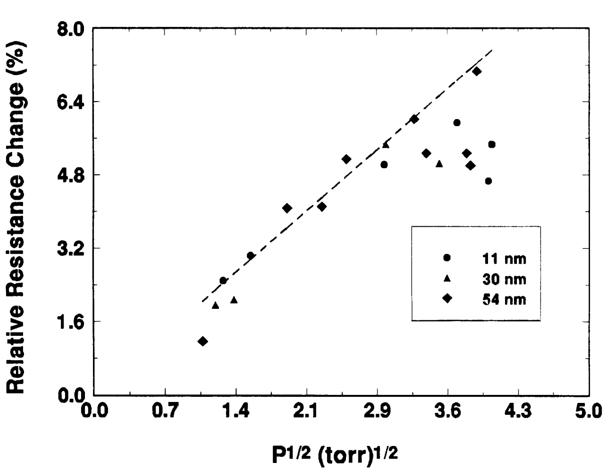

Figure 4. Relative resistance change for Pd films of different thicknesses when exposed to various H_2 pressures ranging between 1 and 16 Torr. (●) Thickness of 11 nm, (▲) 30 nm; (◆) 54 nm.

Pick et al. demonstrated that the resistivity increase in Nb films is proportional to the hydrogen concentration in the film. It can also be easily demonstrated that the hydrogen concentration in the film (at equilibrium and below the critical pressure) is proportional to the square root of the H_2 pressure in the container [4,12,13].

Our results, represented by eq. (8), are in agreement with recent work by Reisfeld et al. [21]. Reisfeld et al. obtained a linear relationship with a slope equal to 2 when plotting relative resistance change as a function of H concentration in a Pd-capped Nb film. This regime corresponds to low hydrogen concentration dissolved in the metal (less than 0.15).

If the final H concentration in the Pd bulk depends on the square root of the H_2 pressure below 8.5 Torr, then we can calculate H concentrations for our experimental conditions. For example, at 2.5 Torr, $x_{max} = 0.08$ and at 4 Torr, $x_{max} = 0.1$ (assuming that $x_{max} = 0.15$ at 8.5 Torr).

Because the curves of the relative resistance change as a function of the square root of the H_2 pressure overlapped for all the Pd films, this strongly indicates that the resistance change is caused by hydrogen in the bulk (resistance change due to surface adsorption decreases inversely proportional to the film thickness).

If the resistance measurements during exposure to the gas are taken at a constant film temperature (for example at 300 K, the Pd bulk resistivity is 1.08×10^{-5} Ω cm), the hydrogen concentration in Pd at saturation of the resistance change can be obtained from the isotherms ($x_{max} = 0.15$ atomic fraction at 300 K). From this information and eq. (8) one can calculate the hydrogen atomic concentration as a function of the resistivity change of the films. This relationship can be useful for making H_2 sensors. Monitoring resistance change in thin Pd membranes can be also useful to determine hydrogen loading during operation conditions.

Resistance change of metallic films when they adsorbed gases is a proven technique to determine the kinetics of adsorption. We have already correlated the results obtained with this technique with TDS experiments: (1) The value of the H_2 desorption energy for the β_1 state in Ni obtained from our TDS experiments [8] agreed well with Shanabarger's results [9,10] using change of resistance measurements; (2) the resistance change of Co films exposed to CO [16], fitted with the expression developed by Pick et al. [12], yielded the same activation energy obtained by means of TDS [8]; (3) Pick, Strongin and coworkers [12–14] performed careful experiments of H_2 adsorption in Nb films measuring change of resistance of the films. Their analyses of the resistance change assumed some H dissolved in the bulk ($x_{max} = 0.0028$) and the kinetics parameters obtained agreed well with values obtained by means of other techniques.

In the present paper, the kinetic of hydrogen absorption by Pd (below $x_{max} = 0.15$) using change of resistance of the Pd film is well correlated with prior TDS data obtained in this system [5–7].

Acknowledgement

This work was supported by FONDECYT 1940696, DIPUC and Fundación Andes. Thanks are due to U.G. Volkmann for helping in the evaporation of the films and to E.G. Silva for TEM inspection of Pd samples.

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