

Structural changes induced by hydrogen absorption in palladium and palladium–ruthenium alloys

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The structural changes in Pd and Pd–Ru alloys induced by the repeated absorption–desorption of hydrogen have been studied. It is found that absorption–desorption cycles produce structural changes in Pd whereas the addition of small amounts of Ru inhibits these hydrogen-induced changes. The experimental results show that bulk hydrogen absorption occurs in Pd, while hydrogen surface adsorption becomes dominant over bulk absorption, in the Pd–Ru alloy. © 1995 American Institute of Physics.

The absorption–desorption process of hydrogen in transition metals is an important issue in catalysis and hydrogen storage. Palladium and palladium alloys play an important role in these processes since these materials have unique diffusion properties for hydrogen. For instance, Pd membranes are used in a variety of hydrocarbon catalytic processes although the details of the processes are not clearly understood. Interestingly, it was shown that the addition of small quantities of ruthenium to Pd enhances the mechanical properties of membranes.¹

We have performed desorption kinetic and structural studies of the diffusion properties of Pd and Pd–Ru alloys. We find that Pd has a high bulk absorption, while in Pd–Ru the initial bulk absorption is low and most of the absorption occurs near the surface. Concomitant with these absorption characteristics, after repeated H absorption cycles, the Pd structure becomes disordered while the Pd–Ru structure remains almost unaltered after cycling. These results are in qualitative agreement with theoretical ideas which imply that bulk hydrogen absorption is controlled by the strength of the hydrogen interaction with the surface of the transition metals, and they also explain the mechanical resistance results found by others.¹

Pd and Pd–Ru membranes were prepared from 0.0025 cm thick foils obtained from Johnson-Matthey Ltd. Gas evolution studies, up to temperatures of 900 K, were performed in a home-built thermal desorption apparatus equipped with a Dycor quadrupole mass spectrometer. In these studies,^{2,3} the sample is heated in ultrahigh vacuum at a constant rate of 10 K/s in a small volume chamber, continuously evacuated. The surface of the foils was cleaned using rinses of methanol and distilled water. Inside the chamber, the typical cleaning procedure was followed: flash desorption in high vacuum up to a temperature of 900 K; and Ar ion sputtering of 1–2 keV for 1–2 min. Auger electron spectroscopy showed that after this cleaning, the surface contamination by Cl, C, and S was less than 1%. The foils were then exposed to 1000 L (1 L = 10⁻⁶ Torr s) of hydrogen at room temperature for the ab-

sorption experiments. X-ray diffraction studies were performed at room temperature using a Rigaku rotating anode diffractometer, before and after gas evolution.

Figure 1 shows the rate of hydrogen desorption (normalized to the maximum value) for a Pd and a Pd–Ru (5%Ru) foil. To obtain a quantitative analysis of these curves a comparison with the standard rate equation theory has been performed.² The rate equation is written as

$$dN/dt = -kN^n, \quad (1)$$

where dN/dt is the rate of desorption, N is the concentration of adsorbed gas, and n is the order of the desorption.

Since adsorbed hydrogen atoms recombine on the surface of transition metals to form the diatomic gas, it follows that the order of the desorption should in principle be $n=2$. Experimentally the order is determined from an Arrhenius plot of the form

$$k = v_n \exp(-E/RT), \quad (2)$$

where k is the rate constant, v_n is the preexponential attempt frequency, E is the activation energy, and R is the gas constant. The constant k is customarily evaluated from the desorption curve.⁴

Within experimental error, this analysis method⁴ gives an excellent fit to the experimental data. The curve for Pd can be fitted by assuming essentially one desorption site. In

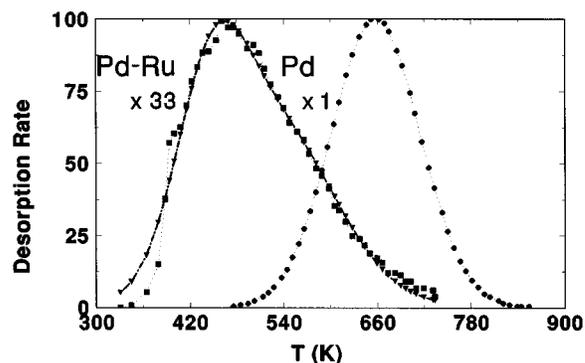


FIG. 1. Hydrogen desorption rates as a function of temperature for Pd (full circles) and Pd–Ru (full rectangles) foils.

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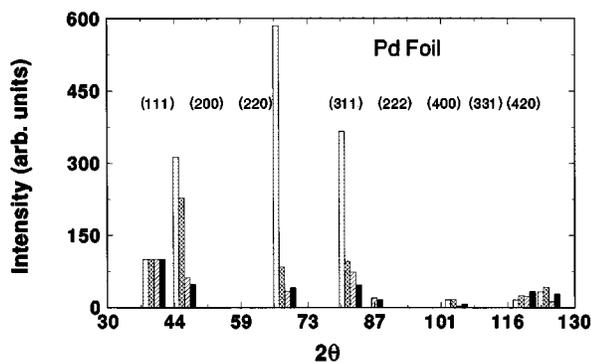


FIG. 2. X-ray intensities of principal x-ray diffraction lines for Pd as a function of treatment.

the case of Pd–Ru, the asymmetry of the peak indicates two desorption sites: one centered at low temperatures which is the dominant feature, and the other at higher temperature near the temperature at which the desorption from Pd occurs. The fit for the Pd–Ru curve, assuming two desorption sites, was obtained and it is represented by the solid line (full triangles) drawn over the experimental curve.

In the case of Pd–Ru, the order of the desorption is $n=2$ indicating that the hydrogen is desorbing from a surface site. On the other hand, the order of desorption for Pd is $n=1.25$, indicating a more complicated process. This type of fractional order of desorption was explained previously⁵ as a consequence of the replacement of desorbing surface hydrogen by bulk hydrogen atoms. The activation energies for desorption are -8.5 ± 0.5 and -10.7 ± 0.5 kcal/mol for Pd and Pd–Ru, respectively. The relative absorption energies obtained from this analysis is in qualitative agreement with prior theoretical work.⁶ This work is based on the idea that the sites close to the surface which bind hydrogen more strongly than sites in the bulk might act as surface valves. This inhibition or enhancement of hydrogen absorption was reported in other experimental work.^{7–10}

Figure 2 shows a comparison of the principal x-ray diffraction (XRD) intensities for different stages of treatment of the Pd foils; the original Pd foil (empty bars), thermal cycling of a foil after 12 temperature cycles (criss-cross bars), thermal cycling of a foil after 12 temperature and after 12 hydrogen desorption cycles (shaded bars), and a standard Pd powder diffraction¹¹ (full bars). The relative intensities imply that the original Pd foil is textured with a strong (220) orientation. A comparison of the relative intensities of Fig. 2 implies that the texture of the foil decreases as the sample is cycled thermally and/or through hydrogen absorption–desorption.

Most importantly, the disorder resulting from the absorption of hydrogen has a stronger effect, the hydrogen treated foils have relative intensities quite close to that expected from a random Pd powder. The immediate conclusion from XRD data and the desorption curves discussed above is that the repeated bulk absorption of hydrogen in Pd tends to destroy the texture.

Figure 3 shows a similar study performed for a Pd–Ru foil. Again the original foil is strongly textured along the (220) direction. In this case however, the change of the x-ray

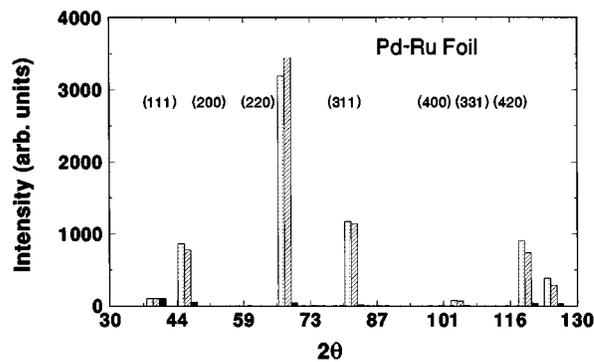


FIG. 3. X-ray intensities for principal x-ray diffraction lines for Pd–Ru as a function of treatment.

intensity peaks is negligible after repeated hydrogen desorption cycles. Apparently the 5% Ru is sufficient to stabilize the texture of the foil. This, combined with the desorption curves, implies that the repeated absorption–desorption of hydrogen on the Pd–Ru surface is incapable of driving strong structural changes of the foil, as occurred in the case of Pd.

The reasons for these radical differences between Pd and Pd–Ru are not completely understood at the present time. The results presented here are in agreement with better mechanical stability observed for the Pd–Ru foils, as mentioned above. It seems that the mechanical stability of the foils is connected with the fact that Pd more easily absorbs hydrogen in the bulk, whereas Pd–Ru absorbs hydrogen mainly on the surface.

The reason for this change of properties may be due to different effects: either (a) the band structure of Pd–Ru at the surface is considerably different,¹² thus, its reactivity towards hydrogen is different or (b) segregation of Ru to the surface may modify the binding energy of hydrogen on the surface with the consequent enhancement of the surface binding energies.

In support of one of the possible effects mentioned above, it has been known for some time that slight coverages of the surface of one transition metal by another may radically change the hydrogen absorption characteristics.⁷

This surprising result may be due to subtle structural changes or surface segregation of Ru and may be the root explanation for the differences in mechanical stability of the foils when exposed to hydrogen. These results have important implications for hydrocarbon catalysis using transition metal foils as membranes.

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