

Thermal diffusivity of palladium-hydrogen systems at room temperature using photothermal detection

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We report results of measurements on the thermal diffusivity, specific heat and electrical resistivity of hydrogenated-palladium samples. It is shown that repetition of the hydrogenation process with the same sample induces aging effects, which lead to erroneous results. The results for the thermal-property measurements on single-cycled palladium samples reflected a phase transition between α -PdH and β -PdH as the hydrogen concentration is increased.

The palladium-hydrogen (PdH_x) system has received renewed interest in the last few years because of the recent attempts to produce the so-called "cold fusion." Even though numerous investigations of the thermal properties of PdH_x systems have been carried out over this century,^{1,2} the effects of hydrogenation cycling on the thermal properties has not been properly addressed in the literature. A critical review of the literature reveals that the great majority of data were obtained with samples that have undergone several hydrogen-absorption and -desorption cycles. In this Brief Report we show that subjecting the same sample to several hydrogenation cycles leads to masked results for the thermal diffusivity and the specific heat of PdH_x samples. These thermal properties were then measured with samples submitted to a single hydrogenation cycle.

A 99.5% pure Pd sample was initially melted in an arc furnace and then cold rolled to produce a Pd foil of roughly 200 μm thickness. The foil was then cut into several square-shaped ($8 \times 8 \text{ mm}^2$) samples. These samples were next annealed at 950 °C for 5 days in an argon atmosphere. This procedure ensured us that the samples used in the experiments had essentially the same initial surface uniformity and malleability. The samples weighing around 700 mg were hydrogenated at a temperature of 100 °C in a computer-controlled stainless-steel cylindrical reactor having 10.9 ml of volume. Before each hydrogenation we carried out an argon flushing to the system. The hydrogen molar concentration ($x = [\text{H}]/[\text{Pd}]$) was varied by injecting hydrogen at different initial pressures and monitoring the hydrogen pressure decay in the reactor as a function of time. For a $x = 0.1$ concentration, we used a hydrogen at an initial pressure of 60 psi, whereas for $x = 0.6$ the initial pressure was around 100 psi. When the desired hydrogen concentration was reached, the microcomputer triggered the controlling solenoid valves to reduce the reactor pressure to 1 atm, and the samples were taken out. The hydrogen content was then double checked by weighing the samples and measuring the mass increase. The error in the pressure measurements were of the order of 10%, and the results agreed quite well with

the ones obtained from the mass measurements. Furthermore, for some of the samples used, we have carried out a third check on the hydrogen content by performing a hydrogen-desorption experiment inside the reactor; the hydrogen concentration was checked from the pressure-rise data. The thin samples prepared by exposing them to hydrostatic H₂ pressure seem to be free of hydrogen concentration gradients.³ A composition which is a function of the distance from the surface is established³ mainly at very high pressures (of the order of 500 psi) and at high hydrogen concentration levels. The low pressures used in this work favor hydrogen diffusion into the sample, thereby leading to a homogeneous sample.

The thermal diffusivity α was measured using a photoacoustic phase-lag method, as described in Refs. 4–6. In Fig. 1 we show the thermal diffusivity of the sample with $x = 0.2$ as a function of the number of hydrogenation cycles; also shown in Fig. 1 are the results for the sample in the dehydrogenated state (i.e., $x = 0$) measured in the intermediate stage between two hydrogenation cy-

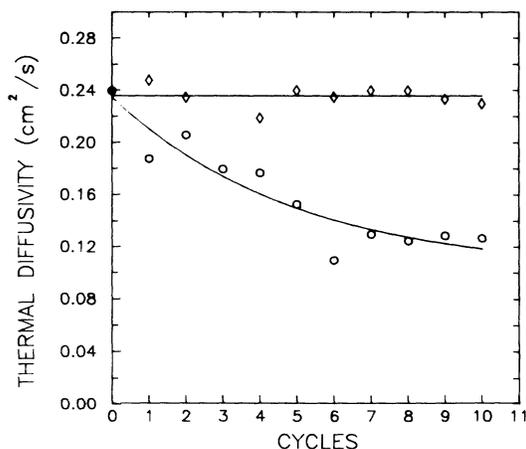


FIG. 1. Thermal diffusivity as a function of the number of hydrogenation cycles for a PdH_x sample with $x = 0.2$ (○) and $x = 0$ (◇).

cles. Figure 1 tells us that, for a hydrogenated sample, the thermal diffusivity decreases quite sharply up to five hydrogenation cycles and tends toward saturation for larger number of hydrogenation cycles. In fact, assuming a first-order kinetics for the dependence of α on the hydrogenation cycle n and performing a data best fit for the $x=0.2$ sample, we found $\alpha=0.133 \exp(-n/4.96) + 0.101$. This result means that α tends to saturate at a value around $0.1 \text{ cm}^2/\text{s}$, and that the number of cycles to approach saturation is of the order of five. The solid line in Fig. 1 for the $x=0.2$ sample corresponds to the above expression obtained from the data best fit. In contrast, the sample with $x=0$ exhibits no aging effect; the constant solid line in Fig. 1 corresponds to the average value of α for the $x=0$ sample. Similar aging effects were also observed in the specific-heat measurements. This result suggests that we should be cautious about the sample history (i.e., how many times it has undergone a hydrogenation process) when measuring the sample thermal properties; otherwise, the sample aging effect may lead to masked results. In view of this we have decided to measure the thermal properties, as a function of the hydrogen content, on freshly single-cycled hydrogenated samples. The results are shown in Fig. 2. The error in these measurements is less than 1.6% with a variance of the order of 4.3%. Up to $x=0.2$ the thermal diffusivity decreases with increasing hydrogen content and stabilizes between $x=0.3$ and 0.5 , where it exhibits a sudden jump to a value of $0.12 \text{ cm}^2/\text{s}$. Above $x=0.5$ the thermal diffusivity exhibits a slow decrease with increasing hydrogen content, reaching a value of $0.105 \text{ cm}^2/\text{s}$ at $x=0.66$. The overall decrease exhibited by the thermal diffusivity as a function of the hydrogen content was of the order 2.3.

To understand the dependence of thermal diffusivity as a function of the hydrogen content, we have measured both the specific heat and electrical resistivity as a function of the hydrogen content. The thermal diffusivity α is defined as

$$\alpha = \frac{k}{dc_p}, \quad (1)$$

where k is the thermal conductivity, d is the density, and c_p is the specific heat at constant pressure. For a metal, k is related to the electrical conductivity $\sigma=1/\rho$ by the Weidmann-Franz law, namely, $k=N_L T/\rho$, where ρ is the electrical resistivity. Using this expression for k , Eq. (1) can be written as

$$\alpha = \frac{N_L T}{d\rho c_p}. \quad (2)$$

The specific heat was measured using the temperature-rise method^{7,8} under continuous white-light illumination, as follows. After being used in the thermal diffusivity measurements, the samples were black coated on both surfaces using a black ink spray and were suspended by a 1-mm-diam nylon lead in a vacuum-sealed Dewar. The Dewar had an optical glass window through which the beam from a 250-W tungsten filament lamp is focused onto the front sample surface. The sample temperature rise was recorded by a thermocouple attached to the back surface of the sample using thermal paste. The specific heat was obtained^{6,7} from the temperature-rise time $\tau=ldc_p/2H$, where l is the sample thickness, $H=4\sigma T^3$, with σ being the Stefan-Boltzmann constant, and T is the ambient temperature. In obtaining c_p from the above procedure, we have used the measured value for the sample density. In fact, the sample-density measurements as a function of x showed that, within the experimental error, the sample density is essentially independent of the hydrogen content and equal to the Pd value, namely, $d=12 \text{ g/cm}^3$.

In Fig. 2 we show the results for the specific heat as a function of the hydrogen concentration. In particular, for $x=0$, the measured value $c_p=0.245 \text{ J/(g K)}$ agrees quite well with the literature value⁹ for Pd. Except for the saturationlike behavior between $x=0.2$ and 0.5 , the overall dependence of c_p on x is essentially linear in agreement with the room-temperature extrapolation of the low-temperature results of Ref. 10. In fact, using the data of Mitacek and Aston,¹⁰ we can write the specific heat of PdH_x samples, at room temperatures as

$$c_p(x) = 0.24 + 0.11x \text{ J/g K}. \quad (3)$$

The solid line in Fig. 2 represents the results of the data linear regression in each characteristic region. The results from the best fit to the data are

$$c_p(x) = \begin{cases} 0.242 + 0.105x \text{ J/g K}, & x \leq 0.2 \\ 0.258 \text{ J/g K}, & 0.2 \leq x \leq 0.45 \\ 0.238 + 0.121x \text{ J/g K}, & x \geq 0.5 \end{cases} \quad (4)$$

We note that, within the 10% experimental error, the fittings in the two linearly increasing regions (for $x \leq 0.2$ and ≥ 0.5) are in good agreement with each other and with the one predicted by Eq. (3).

Finally, we have measured the electrical resistivity as a function of the hydrogen content. The measurements were carried out using the four-probe method with

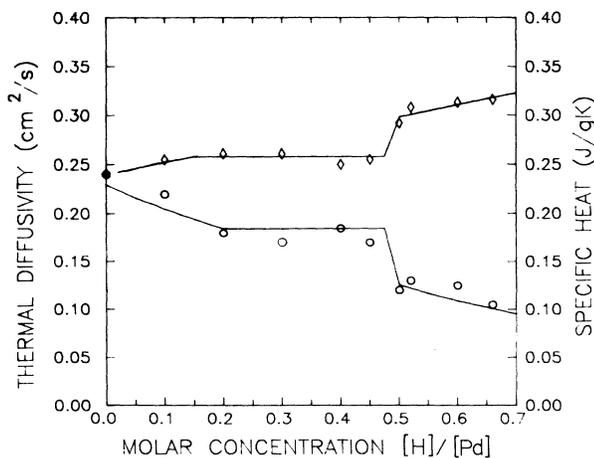


FIG. 2. Thermal diffusivity (\circ) and specific heat (\diamond) of single-cycled Pd samples as a function of the hydrogen molar concentration.

currents of the order of 20 mA. The error in these measurements were of the order of 5%. The results are shown in Fig. 3. As in the case of the specific heat, the resistivity exhibits a linearly increasing dependence on the hydrogen concentration, except for the saturationlike behavior for concentrations in the range between $x = 0.2$ and 0.5. This linear dependence is in agreement with the Mathiessen law for the resistivity of alloys. The solid lines in Fig. 3 are the results of the data linear regression. The results of the best fit to the data are

$$\rho(x) = \begin{cases} 10.96 + 7.85x \text{ } \mu\Omega \text{ cm,} & x \leq 0.2 \\ 12.76 \text{ } \mu\Omega \text{ cm,} & 0.2 \leq x \leq 0.45 \\ 7.27 + 17.96x \text{ } \mu\Omega \text{ cm,} & x \geq 0.5 \end{cases} \quad (5)$$

We note that, unlike the specific-heat case, the two linearly increasing regions of the resistivity have not the same slope. In particular, the slope for the $x \geq 0.5$ region is more than double that of the $x \leq 0.2$ region. We shall return to this point later on. Nevertheless, using Eqs. (4) and (5), together with $d = 12 \text{ g/cm}^3$, in Eq. (2), we have calculated the thermal diffusivity as a function of x . This is shown in Fig. 2 by the solid curve, which, at least qualitatively, agrees with the experimental data.

The sudden jump observed in the measurements of α , c_p , and ρ around $x = 0.5$, following the plateau between $x = 0.2$ and 0.45, is attributed to the phase transition between α -PdH and β -PdH. In fact, x-ray- and neutron-diffraction data¹¹⁻¹⁴ indicate that the occlusion of hydrogen produces two different phases in the palladium lattice, namely, the α and β phases. In both, the structure of the Pd lattice is fcc with different lattice parameters, and the hydrogen atoms occupy interstitial octahedral sites. The distribution of α and β phases in a PdH_x system has been discussed by Nelin.¹⁴ It is shown that it depends on the actual temperature and hydrogen-gas pressure used in the hydrogenation process. Above 310°C the phase is always pure α phase, and below this temperature pure α and β phases exist only at low and high concentrations, respectively. At intermediate concentrations the two phases coexist. The coexistence of these two phases is more pronounced in the concentration range between 0.15 and 0.45. Above $x = 0.5$ the PdH_x system is predominantly in the pure β phase. The overall behavior of the thermal diffusivity as a function of x shown in Fig. 2 seems to reflect this α - to β -phase transition. Up to $x = 0.2$ the thermal diffusivity decreases as a result of the increases of both c_p and ρ with increasing hydrogen concentration. Between $x = 0.2$ and 0.45 the system undergoes the phase transition and the two phases coexist. Above $x = 0.5$ the PdH_x system is in the β phase and the thermal diffusivity continues to decrease again. The decrease of α in this case is, however, slower than that in

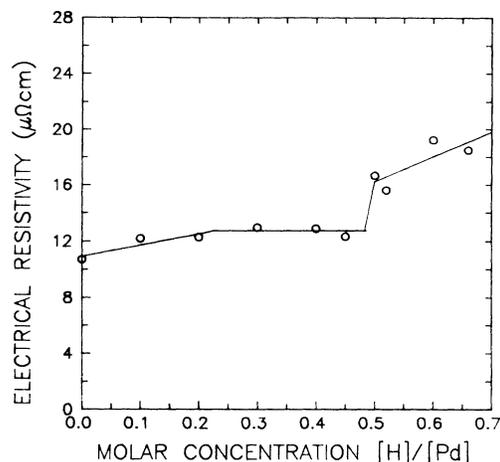


FIG. 3. Electrical resistivity of single-cycled Pd samples as a function of the hydrogen molar concentration.

the α phase. This is due to the fact that the electrical resistivity in this region increases at a faster rate than in the α phase, as evidenced in Fig. 3. The specific heat, however, increases at roughly the same rate in both phases.

In conclusion, we have investigated in this Brief Report the photoacoustic measurement of the thermal diffusivity of PdH_x samples as a function of the hydrogen content. It was shown that to get reliable data of both α and c_p , one should work with single-cycle hydrogenated samples; otherwise, aging effects may produce misleading results. Even though the observations of mechanical deformations due to hydrogenation cycling has been reported in the literature,¹ the influence of aging effects on the thermal diffusivity has not been discussed so far. The present results indicate that one should always work with samples produced following the same preparation procedure. The photoacoustically measured thermal diffusivity was interpreted as reflecting the α - to β -phase transition that takes place in PdH_x with increasing hydrogen concentration. The effect of the hydrogen concentration gradient as a possible explanation for the observed plateau in the physical properties between $x = 0.2$ and 0.45 may be ruled out by two arguments. First, the hydrogenation pressures and concentrations were low enough to prevent a concentration gradient. Second, if a concentration gradient were present, one would observe an average behavior of a bulk property which would tend to smooth out the well-defined plateau as shown in Figs. 2 and 3. Finally, we emphasize that the observed plateau occurred at the concentration range where both x-ray- and neutron-diffraction data indicate the coexistence of phases α and β .

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