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In situ measurement of elastic properties of PdH_x, PdD_x, and PdT_x

Arnaud Fabre[a,b], Eric Finot[a,*], Jérôme Demoment[b], Serge Contreras[b]

[a]*Laboratoire de Physique, UMR CNRS 5027, Université de Bourgogne, F-21011 Dijon, France*
[b]*Commissariat à l'Energie Atomique, Département de Recherche sur les Matériaux Nucléaires, F-21120 Is/Tille, France*

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Abstract

The Young's modulus *E* of palladium hydride PdH_x, deuteride PdD_x and tritide PdT_x were measured for studying the effect of both hydrogen stoichiometry *x* and isotope nature. A special technique based on optical detection of flexural modes of a palladium cylindrical microcantilever was adapted to in situ measurements to guarantee the sample homogeneity during the hydriding process. A 10% decrease in *E* was found between pure polycrystalline palladium and hydride phases. The non linear dependence observed with the H content was discussed in terms of lattice expansion, phonons and electronic properties. Sensitivity of the technique enables to distinguish an isotope effect on *E*.

Keywords: Palladium hydrides; Microcantilever; Elasticity; Young's modulus

1. Introduction

Considerable attention has been given to devices suited to safe hydrogen isotope storage, especially tritium. Palladium hydride fulfils conditions of density (7 NTP l of H_2 per cm^3 of palladium) and safety (low hydride equilibrium pressure of $5 \cdot 10^3$ Pa at room temperature) [1]. In the case of tritium, understanding the aging process is of prime importance to control the storage performance.

The hydriding process is known to affect the initial properties of the host metal, especially the mechanical properties [2–6]. Inserting hydrogen into the octahedral sites of the palladium f.c.c. lattice expands the lattice in linear proportion to the hydrogen content [7]. The dislocation density increases during the hydriding process for accommodating the lattice distortions induced by the coexistence of phases, thereby causing the emergence of fractures [8]. In the case of tritides, the natural radioactive decay of tritium, which produces helium-3 atoms in the host lattice, should also be considered. Since helium atoms are insoluble in palladium, like in most metals, they tend to gather into bubbles of nanometric size [9,10]. The high bubble pressure stresses the lattice and causes the lattice swelling [11,12]. Modeling the growth of these helium bubbles requires some experimental results such as elastic moduli. The Young's modulus of the palladium tritide is unknown because usual methods are not suitable for tritium environment. In situ measurements under a tritium atmosphere are required to ensure the homogeneity of the tritide. A new approach, based on the detection of vibrational modes of microcantilevers has been applied. Exposure of palladium samples to hydrogen induces a change in elastic properties thereby causing a resonance frequency shift. This in situ method enables one to monitor the change in elastic properties with respect to the hydrogen content and the isotope nature.

2. Experimental

The measurement method was previously described elsewhere [13]. Briefly, the experimental setup is based on the periodic excitation of the fixed end of a cylindrical cantilever and the detection of its natural resonant frequency *f*. Measuring *f* and assuming geometry and density of the sample known permit one therefore to determine the Young's modulus *E* from the following:

$$E = \frac{4}{3} \cdot \left(\frac{\pi L^2 f}{r} \right)^2 \rho \qquad (1)$$

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*Corresponding author. Laboratoire de Physique de l'Université de Bourgogne, Equipe Optique Submicronique, UFR Sciences et Techniques, 9 Rue A. Savary, B.P. 47870, 21011 Dijon, France. Tel.: +33-3-8039-3774; fax: +33-3-8039-6024.

E-mail address: eric.finot@u-bourgogne.fr (E. Finot).

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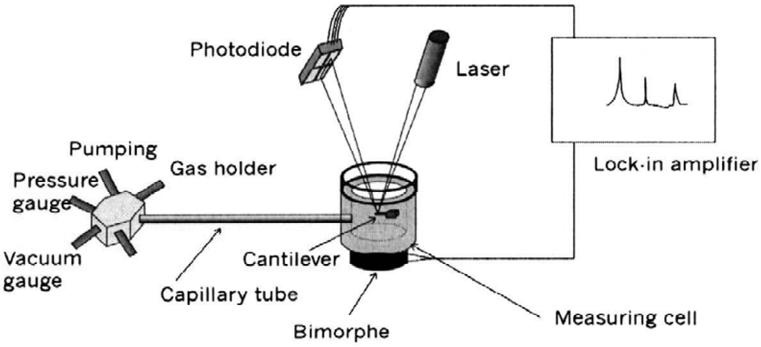

Fig. 1. Experimental setup.

where L is the length, r is the radius, and ρ is the mass density of the cantilever.

An activation process is necessary before charging palladium samples with hydrogen. This operation consists of degassing the palladium surface by heating the sample under a secondary vacuum. Correct activation requires a secondary vacuum for 2 h at 150 °C [14].

A special cell holding the cantilever has been developed to withstand pressures ranging from a secondary vacuum to almost 1.5 MPa (see Fig. 1). The cell made of aluminum alloy has an internal volume of 0.5 cm^3. A metallic tube of 15 cm in length and 1 mm in diameter allows pumping and the gas introduction to the cell. A vacuum of 10^{-2} Pa is achieved at the input of the capillary tube in less than 30 min. Cantilever temperature is maintained using a warming wire rolled around the cell previously calibrated in temperature. Because they react with hydrogen, piezoelectric transducers used to transmit the energy to the cantilever were glued on the lower external part of the measuring cell.

The gas pressure P is monitored using a gauge (0–1 MPa, TransInstruments). f is determined using a position sensor detection instrument connected to a lock-in amplifier (SR 850, Stanford Research Systems) for extraction and averaging.

Determining f is accurate within 0.01%. As the accuracy in elasticity measurements depends mainly on the cantilever design, the length L_0 and the radius r_0 of each cantilever were measured using scanning electron microscopy (SEM). The samples used in this study were palladium cylindrical cantilevers (Goodfellow). Since the grain size of the samples is centered to 1 μm, diameters of the cantilevers was fixed to $r_0 = 125$ μm in order to ensure the assumptions of the continuum mechanics [13].

3. Results and discussion

The reliability of this technique has already been proven on palladium samples [13,15]. For this study, cantilevers of cylindrical shape are preferred to rectangular ones in order to avoid any surface stress problems causing the bending of the sample.

Prior to palladium activation, measurements performed under vacuum permit one to determine a Young's modulus of 128±3 GPa for pure palladium, which is consistent with results from the literature concerning polycrystalline palladium [2–4]. X-Ray measurements have also been performed on our samples to determine the grain orientations and calculate the elastic constant tensor of our polycrystalline palladium cantilevers via an autocoherent model [15]. A Young's modulus of 127 GPa was then calculated in the direction of the thickness of cantilevers, thereby confirming the reliability of the method.

The next step was to expose palladium cantilevers to hydrogen. The hydride stoichiometry x was obtained from the pressure drop within the cell ΔP_x by:

$$x = \frac{n_{\mathrm{H}}}{n_{\mathrm{Pd}}} = \frac{2V}{RT} \cdot \frac{M_{\mathrm{Pd}}}{\rho_{\mathrm{Pd}}} \cdot \frac{\Delta P_x}{V_0} \qquad (2)$$

where n_{H} is the number of hydrogen moles absorbed within palladium (note that $n_{\mathrm{H}} = 2n_{\mathrm{H2}}$), n_{Pd} is the number of palladium moles, V is the gaseous volume surrounding the palladium cantilever (equals to 4.6±0.5 cm^3), V_0 is the cantilever volume, $T = 298 \pm 2$ K, ΔP_x is the loss of pressure within the cell during hydriding, $R = 8.314$ J mol^{-1} K^{-1} and $M_{\mathrm{Pd}} = 0.10642$ kg mol^{-1} [16]. The density ρ_{Pd} of our polycrystalline samples was measured at 12830±130 kg m^{-3} using a microgram balance. Note that ρ_{Pd} differs from the literature value of the single crystal, which is around 12000–12100 kg m^{-3} [16,17].

Let us consider a cylindrical cantilever with $L_0 = 3.600 \pm 0.005$ mm and $r_0 = 250 \pm 5$ μm, namely $V_0 = 0.71 \pm 0.015$ mm^3. After hydrogen introduction to the cell, P decreases from $2.05 \cdot 10^5$ Pa to an equilibrium value of $1.91 \cdot 10^5$ Pa in 160 min as shown in Fig. 2. A hydrogen stoichiometry of 0.65±0.05 was then obtained at the end of the absorption which means that the palladium cantilever is totally hydrided in the β-phase after 160 min of hydrogen exposure.

From a microscopic point of view, insertion of hydrogen expands the palladium lattice but also hardens the proton-

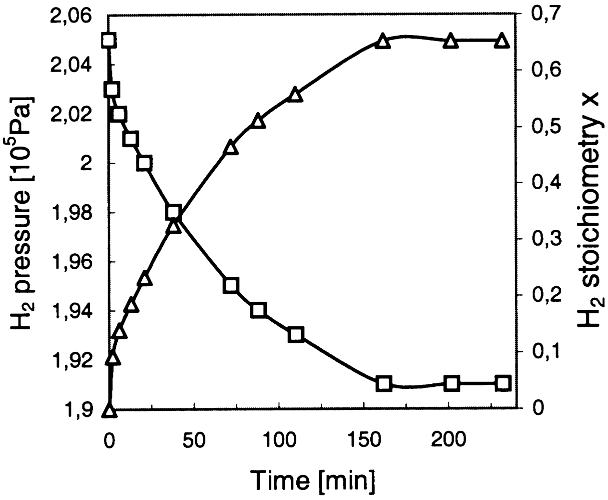

Fig. 2. H_2 pressure drop in the cell (squares) and hydride stoichiometry (triangles) as a function of time for cylindrical cantilever.

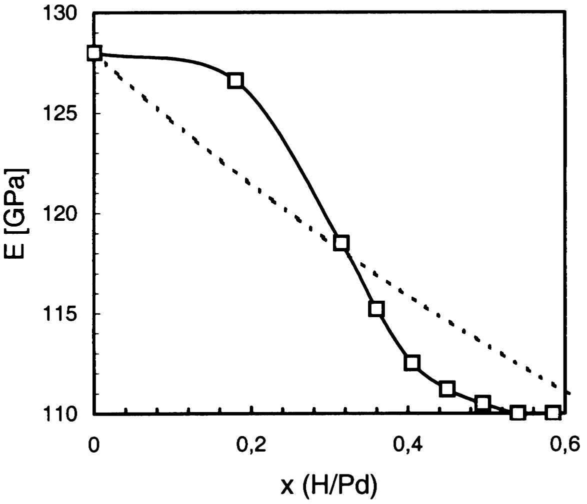

Fig. 3. Experimental Young's modulus (squares) with respect to stoichiometry and calculated Young's modulus from a Reuss model (dashed line).

palladium potential, and these two behaviors could have antagonistic effects on E. The expansion is known to be isotropic and linear with change in x [7]. For $x=0.66$, the lattice expands by 11.2% in volume, corresponding to a decrease in density to $\rho_{0.66}=11680$ kg m^{-3}. The Young's modulus of the hydride E_x is therefore a function of x as:

$$E_x = \left(\frac{2\pi L_x^2 f_x}{r_x}\right)^2 \cdot \frac{\rho_x}{3} = \frac{4\pi^2}{3} \cdot \left(\frac{(1 + x\frac{\Delta a_H}{a_H})L_0^2 f_x}{r_0}\right)^2 \rho_x \qquad (3a)$$

with

$$\rho_x = \left(\frac{1 + \frac{m_H}{m_{Pd}}x}{1 + 3\frac{\Delta a_H}{a_H}x}\right)\rho_0 \qquad (3b)$$

where f_0 and f_x are the resonant frequencies for Pd and PdH$_x$, respectively, L_0, r_0 and L_x, r_x stand for the lengths and radius of Pd and PdH$_x$, respectively, $\Delta a_H/a_H=5.33\cdot10^{-2}$, $(\Delta a_D/a_D=5.60\cdot10^{-2}$ for deuterium and $\Delta a_T/a_T=5.60\cdot10^{-2}$ for tritium), $m_H=1.008$ g mol^{-1} ($m_D=2.015$ g mol^{-1} for deuterium and $m_T=3.017$ g mol^{-1} for tritium), and $m_{Pd}=106.42$ g mol^{-1} [7,16].

For palladium hydride PdH$_{0.66}$, $E_{0.66}$ was measured at 110±5 GPa. As a result, E decreases by 15% from the pure metal phase to the β-phase. Change in E seems to be more pronounced for a polycrystal than for a single crystal which looses 10% in its elastic constant as measured using ultrasonic technique by Hsu and Leisure [6]. The decrease indicates that the lattice expansion is maybe predominant against electronic considerations. Fig. 3 shows the decrease of E as a function of x. Most of the change in E occurs in the plateau region of the palladium (P–C–T) diagram. As the β-phase grows within the α-phase of palladium, E is the resulting Young's modulus of a two-phase material. From a composite mechanics point of view, the transverse Young's modulus of the whole material can be evaluated by a Reuss model as a function of the β-phase proportion:

$$E = (V_\alpha + V_\beta) \cdot \left(\frac{V_\alpha}{E_\alpha} + \frac{V_\beta}{E_\beta}\right)^{-1} \qquad (4)$$

with V_α the volume fraction of the α-phase, the volume fraction of the β-phase $V_\beta=[1+3(\Delta a/a)x]\cdot(1-V_\alpha)$ because of the swelling due do the insertion of hydrogen in the lattice, E_α and E_β the Young's moduli of the α and β-phases, respectively. As reported in Fig. 3 in which E_α and E_β were fixed at 128 and 110 GPa, respectively, the model predicts a non-linear behavior of E with stoichiometry. However, this non-linearity exhibits both an inflection point and a gap with the linear behavior unpredicted by a simple Reuss model which makes no hypothesis upon the phase morphology. Thus, the behavior observed for our palladium samples cannot be only explained by the fact that two phases constitute the material.

An elastic constant C_{ij} consists of a frozen lattice contribution C_{ij}^0 and a phonon contribution C_{ij}^{ph}. Concerning optical phonons, Geerken et al. [18] have proposed a tractable expression of C_{ij}^{ph} using a quasi-harmonic model but this contribution was found to be linear with x. Although C_{ij}^{ph} depends on the temperature, change involved in the exothermic process of hydriding is not large enough to affect C_{ij}. C_{ij}^0 is related to the lattice parameter and electronic band filling. The expansion of the palladium sample is experimentally known to vary linearly with x, so the non-linearity of E with x can be rather related to electronic phenomena.

Calculation of electronic states of substoichiometric palladium hydrides showed a non-linear dependence with x of some quantities, especially the average density of states on the hydrogen sites [19]. Electronic affinity of H in the palladium lattice could be considered as a factor for explaining the non-linearity of E over x. However, note that for stoichiometries x^* corresponding to the plateau region (approximately $0.1 < x^* < 0.6$ at room temperature), palladium hydride is a mixture of the α and β phases, neither of them having a concentration of x^*, while the calculations consider a non realistic hydride of stoichiometry x^*. Thus, calculations are only indicative. Although the electronic contribution must have a significant role in the changes of elastic properties, it appears difficult here to distinguish the different contributions to the elastic moduli.

Finally, the same kind of experiments were carried out with deuterium and tritium instead of hydrogen. Note that tritium handling required the installation of the experimental setup within a glove box. As shown in Fig. 4, the extreme sensitivity of the palladium cantilevers permits one to determine an isotope effect on the Young's modulus when isotope exchanges were performed on a same sample. The isotope exchange experiments enable to obtain a great accuracy on E between the different isotopes because during experiments, no phase transitions $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ occurred, thereby not disturbing the mechanical behavior of the cantilever. The Young's moduli of the hydride, of the deuteride and of the tritide are 112, 117 and 119 GPa, respectively. Experimental results appear to be consistent because there is a gradual progression in E from the hydride to the tritide. The fact that E for tritide and deuteride are close is not surprising since many properties show the similar isotope dependence. Ex situ ultrasonic measurements [18] on single crystal of palladium showed that elastic constants of the hydride C_{44}, C' and C_L are higher than that of the deuteride. Differences between these two results could arise from experimental conditions since our measurements were performed on polycrystals under hydrogen pressure.

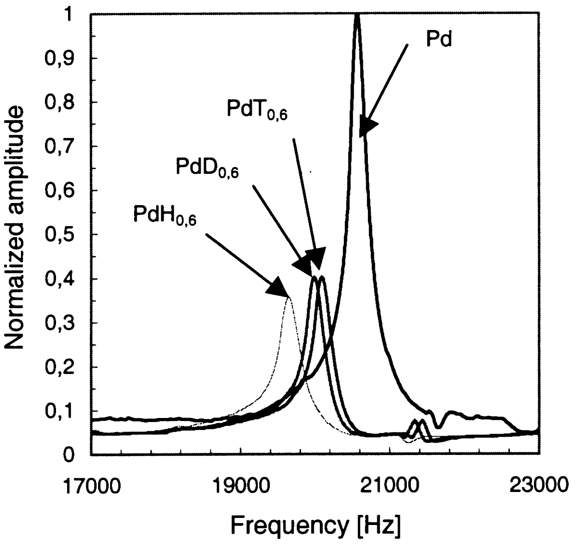

Fig. 4. Resonance frequency peaks of cylindrical palladium cantilever under vacuum, hydrogen, deuterium and tritium.

Let consider the factors responsible for this isotope effect. The lattice expansion and the phonon frequencies may affect the elastic moduli of the three different isotopes. The transverse phonon frequencies are quite different between hydride, deuteride and tritide because of the high relative mass difference: $\omega_t^H = \sqrt{2}\omega_t^D = \sqrt{3}\omega_t^T$. Finally, it is worth noting that since all theoretical aspects concern single crystal, there is consequently one more step to go when considering polycrystals.

4. Conclusion

This in situ study revealed a non-linear decrease of the Young's modulus with increasing hydrogen content in palladium hydride. The electronic contribution to the elastic moduli and the mechanical coexistence of the two phases mainly explained this experimental fact since other contributions as the lattice expansion varies in linear proportion with the hydrogen content. Moreover, an isotope effect was determined between hydride, deuteride and tritide, thereby indicating the importance of the lattice expansion and the phonon frequencies to the elastic moduli of materials.

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