Journal of Alloys and Compounds 500 (2010) 1–4

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Strain and resistivity of PdH_x at hydrogen composition $x > 0.8$

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ARTICLE INFO

Article history:
Received 18 February 2010
Received in revised form 20 March 2010
Accepted 25 March 2010
Available online 2 April 2010

Keywords:
Palladium wire
Stoichiometry
Hydrogenation
Electrolysis
Resistivity
Strain

ABSTRACT

Measurements of lattice expansion and electrical resistance versus hydrogen concentration, $x = H/Pd$, in a continuous range of stoichiometry $[0 \leq x \leq 1.16]$ in the PdH_x stretched system have been performed. High hydrogen compositions were achieved using electrochemical H loading procedure which allowed stable PdH_x systems to be obtained.

Strain of only 1.2% from pure Pd to $PdH_{1.16}$ due to the isotropic lattice expansion has been reported; the observed trend is in disagreement with the scant literature data available. The resistivity of PdH_x system in function of H content has been also investigated and discussed.

1. Introduction

In our previous paper [1], a series of hydrogenation/dehydrogenation cycles on palladium wire samples, stressed by a constant tension have been performed. A large increase of palladium electrical resistivity due to the combined effect of the defects production linked to hydrogen diffusion inside the host lattice and the stress applied to the sample has been reported. An increase of the palladium sample strain due to hydrogenation/dehydrogenation cycles in $\alpha \rightarrow \beta \rightarrow \alpha$ phase transitions, compared to the sample only stressed without hydrogen cycles, has been observed. The loss of initial metallurgical properties of the sample occurs already after the first hydrogen cycle.

In the previous paper [2], the effect of hydrogen content on the strain and on the electrical resistivity of a Pd sample stressed by a constant tension has been investigated in a series of hydrogenation cycles and in a continuous range of H stoichiometry $[0 \leq x \leq 0.8]$. A strain of only 1% from pure Pd to $PdH_{0.8}$ due to the isotropic lattice expansion has been reported for both "as drawn" and "annealed" Pd sample, in disagreement with literature data available. It was found that this effect is minimum at $x = 0.13 \pm 0.06$ ($\alpha + \beta$ phase), and increases from $x = 0.6$ (β phase).

Data regarding the strain for corresponding H/Pd ratios is well known up to a concentration of $H/Pd < 0.7$ [3–11]. On the contrary, only exiguous and contrasting data for the physical behaviour of the lattice expansion corresponding to loading ratios greater than $H/Pd = 0.7$ [3] is available.

In this paper we focalize our study in a continuous range of stoichiometry between $x = 0$ (α phase) and about $x = 1.2$ (γ phase), investigating the effect of hydrogenation on the lattice expansion and on the electrical resistivity variation.

2. Experimental considerations

Hydrogen (H) has been loaded into the palladium (Pd) lattice electrochemically using this metal as cathode and platinum (Pt) as anode. The cathodes used for all the experiments are Pd wires of the same batch (LS266962 AVS PD005116/6) at 99.9% purity grade (Goodfellow) as received ("as drawn") with 50 μm in diameter and 6.5 cm long. The anode is a Pt rod at 99.995% purity grade (Goodfellow) with 1 mm in diameter and 6.5 cm long. The experiments are conducted in controlled environment at 293 K. The aqueous electrolytic solution is made with, $SrSO_4$ anhydrous, general purpose grade (Fisher Scientific) at 10^{-4} M and Hg_2SO_4 at 10^{-5} M, with ultrapure water at more than 18 MΩ cm, purified by the system "Elix-5/Milli-Q" (Millipore). Hydrogenation and dehydrogenation, in potentiostatic mode, consists respectively in cycles of cathodic H loading (150 V) and anodic H de-loading (60 V). Hydrogenation current is about 25 mA (for 150 V) and dehydrogenation current is about 10 mA. The ac electrical resistance of the Pd wire is measured during the electrolysis using the standard four-probe technique with an RLC meter at frequency of 1 kHz. The high impedance of the solution avoids parasitic effect on the ac electrical resistance measurement of the Pd wire. The elongation of the wire during loadings and its contraction during de-loading are measured during electrolysis. The Pd wire is maintained in a vertical position by a constant mechanical tension applied. The set-up and the electrolytic cell used in this work have been described elsewhere [1,2].

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doi:10.1016/j.jallcom.2010.03.197

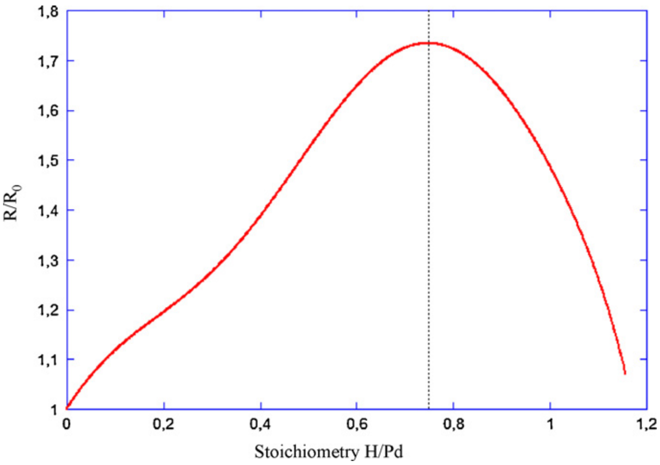

Fig. 1. Relative resistance R/R_o changing versus H stoichiometry $x = H/Pd$ for PdH_x sample at room temperature. R_0 is the resistance of pure Pd sample at stoichiometry $x = 0$. The region between $x = 0$ and $x = 0.75$ is based on the Refs. [12,13], while the region $x > 0.75$ on Refs. [14–16].

3. Results

The objective of these experiments is to study, for a continuous range of stoichiometry, the effect of hydrogen content on the lattice expansion and on the electrical resistivity variation of PdH_x samples for very high H stoichiometry x.

Hydrogen was loaded into the palladium lattice using an electrochemical cell. This method allows high H/Pd concentrations to be achieved at room temperature and pressure.

The experiments were performed with the Pd wire described in Section 2, stressed by a constant mechanical tension $T \approx 0.22$ N, equivalent to an initial pressure of about 114 MPa.

The H/Pd concentration was not directly measured during the electrochemical loading, but was obtained indirectly by correlating the relative resistance ratios R/R_o of the PdH_x system versus $x = H/Pd$ concentration, where R_o is the pure Pd electrical resistance, Fig. 1.

At room temperature, this curve has a maximum at $x \approx 0.75$ and then it decreases almost to the initial value at $x \approx 1.2$. The region between $x = 0$ and $x = 0.75$ is based on the experimental reported data [12,13], while the region $x > 0.75$ is based on references [14–16].

As shown in Fig. 1, a polynomial function can be used to fit the resistance ratio R/R_o as a function of $0 \leq x \leq 1.16$. By this correlation, it is possible to determine the average stoichiometry H/Pd from our instantaneous relative resistance measurements with an error $\Delta(H/Pd) = 0.06$.

The advantage to determine the H content dissolved in Pd lattice by electrical resistance measurement is that the resistance reflects the overall bulk properties of the sample affected by the hydrogen adsorption, so it does not depend on the local characteristics and surface impurities; for this aim during electrolysis the four-probe ac resistance measurements of the palladium electrode were performed using 1 kHz sinusoidal current.

Fig. 2 shows the relative resistance measurement R/R_o (□ red) and the relative length variation $\varepsilon = \Delta l/l_0$ (○ blue) of Pd wire versus time during the hydrogenation/dehydrogenation cycle; l_0 is the initial Pd wire length at stoichiometry $x = 0$. Two different regions are reported: the R/R_o behaviour during 150 V cathodic H loading and R/R_o behaviour during 60 V anodic H de-loading of the Pd wire. The maximum value of stoichiometry H/Pd = 1.10 corresponding to $R/R_o = 1.25$ is achieved in about 200 s.

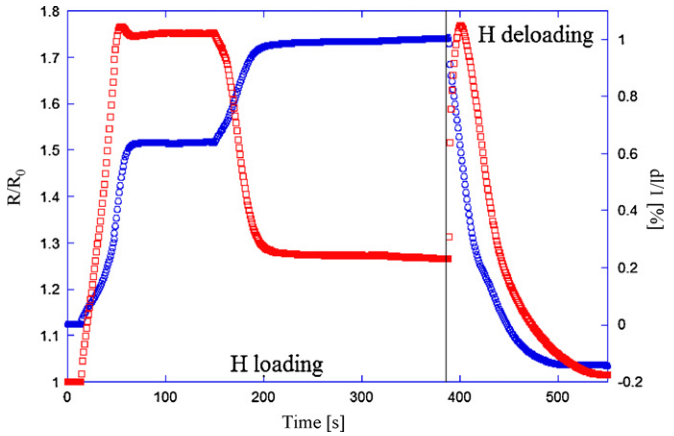

Fig. 2. Relative resistance R/R_o (□) and relative elongation $\varepsilon = \Delta l/l_0$ (○) during H loading and de-loading of PdH_x system changing versus time at room temperature. l_0 is the initial Pd wire length at stoichiometry $x = 0$.

As expected [3], in Fig. 2, an expansion of the host lattice (strain $\varepsilon = \Delta l/l_0$), while the hydrogen concentration increases, is observed. The sensitivity of the set-up is so high that at the end of the hydrogenation region a very little increase of hydrogen stoichiometry causes a visible increase of the lattice dimension.

When an H/Pd equilibrium concentration is obtained (stable R/R_0), no lattice dimension variation is observed. The reverse behaviour is found during H de-loading.

In this paper, we focalize our study in a continuous range of stoichiometry between $x = 0$ and about $x = 1.2$ [15], investigating the effect of hydrogenation on the lattice expansion and resistivity.

Instantaneous measurement of the relative resistance, R/R_o, and of the variation of the sample length, Δl, allows to investigate the expansion of the Pd wire, $\varepsilon = \Delta l/l_0$, with a maximum error of 0.01%, for corresponding H/Pd ratios, Fig. 3.

In Fig. 3, the values of strain ε versus stoichiometry for three different Pd samples are plotted. The continuous curve represents the best fit of the experimental data with a correlation coefficient of 99.86%. Data shows that the elongation of a PdH_x sample is an increasing monotone function of the hydrogen content. Te trend is not completely linear, in contrast to the literature data available [3]. Since Pd has an fcc structure, the H insertion has an isotropic effect on the expansion of the Pd lattice ($\Delta l/l_0 = \Delta a/a_0$). According to these data, the hydrogen adsorption causes an increasing of the Pd lattice constant, a, of $1.20 \pm 0.01\%$ passing from a stoichiometry $x = 0$ to $x = 1.16 \pm 0.06$. Using the Pd lattice constant $a_0 = 3.890$ Å [17] for the $PdH_{1.16}$ alloy, corresponds $a = 3.937$ Å. This value is in disagreement with the literature data available [3–9], which shows

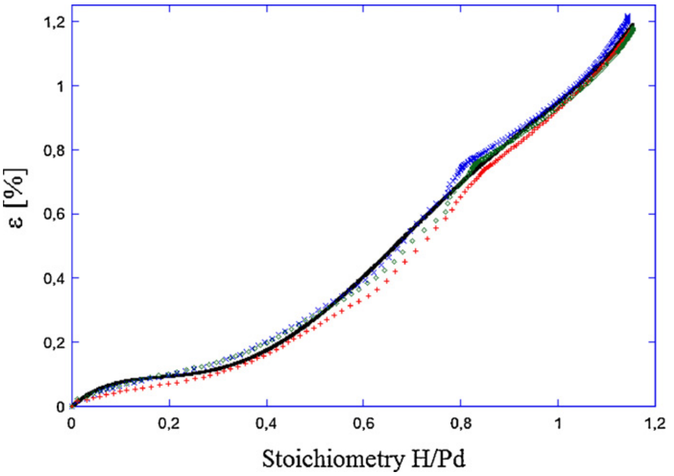

Fig. 3. Relative elongation $\varepsilon = \Delta l/l_0$ and fit (continuous line) for three different Pd samples in function of the H loading stoichiometry (maximum error on ε is $\pm 0.01\%$).

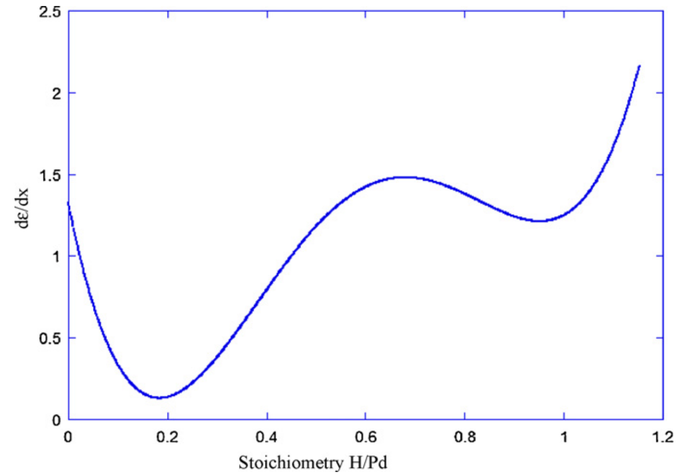

Fig. 4. Differential variation of the Pd lattice constant, $d\varepsilon/dx$, (fit of Fig. 3) in function of the H loading stoichiometry.

an increase of the lattice constant of about 4% for the stoichiometry $x = 0.8$.

Fig. 3 shows that for H/Pd ratios of about 0.2 the effect of hydrogen insertion on the physical behaviour of the Pd lattice expansion is very low. Moreover for H/Pd > 0.7 a quite linear behaviour is observed, which disagrees with Ref. [3] where a drop of the curve's slope is reported.

Fig. 4 shows the differential variation of the Pd lattice constant, $d\varepsilon/dx$, in relation to x = H/Pd concentration; for H/Pd ratios of about 0.2 the insertion of hydrogen into the host lattice causes a very low modification of the lattice constant, moreover for $x > 0.2$ the differential variation is an increasing function, except in the window $0.7 < x < 0.95$, where a little decreasing is observed. For very high H/Pd ratios, the $d\varepsilon/dx$ increases exponentially, meaning that a little increase of hydrogen concentration causes a huge increase of the lattice constant.

During the hydrogenation of a palladium wire, its electrical resistance is a function of the dimensional properties of the sample (length l and cross section S) and of the electron scattering centers (resistivity ρ):

$$R(x) = \rho(x) \cdot \frac{l(x)}{S(x)} \tag{1}$$

As assumed before, the H insertion has an isotropic effect on the Pd lattice expansion in the three axis directions x, y, z. Considering the length of the wire in the z axis:

$$\frac{\Delta l_x}{l_x} = \frac{\Delta l_y}{l_y} = \frac{\Delta l_z}{l_z} \Rightarrow \frac{\Delta S}{S} = \frac{\Delta l_x}{l_x} + \frac{\Delta l_y}{l_y} = 2 \cdot \frac{\Delta l_z}{l_z} = 2 \cdot \varepsilon \tag{2}$$

the cross section S of the hydrogenated sample can be determined from ε by using the Eq. (2).

From the length and the resistance measurements, together with the determined cross section (SEM analysis: Jeol-JSM-6320F), it is possible to calculate the electrical resistivity in function of the H concentration inside the host lattice.

The normalized resistivity (maximum error of 0.01) in relation to hydrogen content for the H loading of the samples (examined in Fig. 3) is plotted in Fig. 5.

Since in Fig. 2 the maximum values of relative resistance are similar during the hydrogenation and the dehydrogenation of the Pd lattice, not a high electrical resistivity variation is expected between H loading and de-loading processes.

Fig. 6 shows the differential variation of the Pd electrical resistivity, $d(\rho/\rho_0)/dx$, in relation to x = H/Pd concentration; from H/Pd ratios of 0 to about 0.75, the insertion of hydrogen into the host lattice causes an increase of the Pd resistivity; this effect has a relative minimum at a concentration of about 0.2 (as it happens for the lattice expansion). For $x = 0.75$, a little insertion of hydrogen into the host lattice causes no variation of the Pd resistivity. In the window $0.75 < x < 1.16$, a strong decreasing rate of the resistivity in function of the hydrogen content is observed. Moreover, a drop of such slope is observed for $x > 1$. No theoretical model is documented in literature that can explain the relationship between the curves of the resistivity and the strain in function of the H stoichiometry.

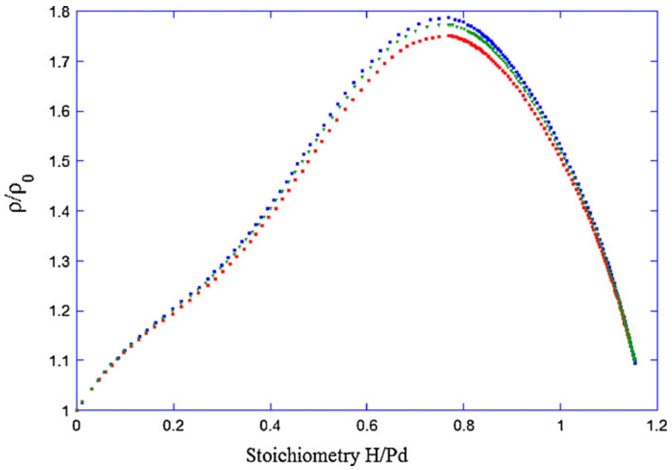

Fig. 5. Normalized resistivity in function of H loading stoichiometry for the three samples of Fig. 3.

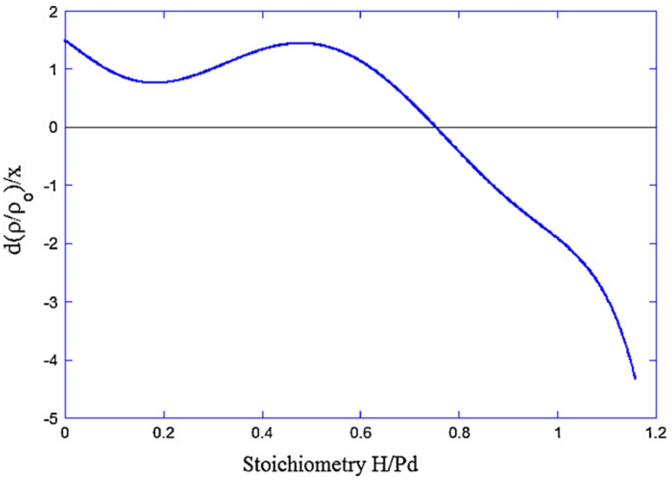

Fig. 6. Differential variation of the normalized Pd electrical resistivity, $d(\rho/\rho_0)/dx$, (fit of Fig. 5) in function of the H loading stoichiometry.

4. Conclusion

The effect of hydrogen content on the relative elongation and on the electrical resistivity of a stretched Pd sample has been investigated for a continuous range and very high H stoichiometry x $[0 \le x \le 1.16]$.

The expansion of the Pd lattice was found to be an increasing monotone function in respect to hydrogen content up to a strain of about 1.2% at the maximum concentration investigated ($x = 1.16$); considering an isotropic lattice expansion, the lattice constant passes from $a = 3.890$ Å for pure Pd to $a = 3.937$ Å for $PdH_{1.16}$. This lattice expansion contradicts literature data available (which show elongation of about 4% for $PdH_{0.8}$). No drop of the curve's slope is observed for $x > 0.7$, as reported in literature. The effect of hydrogen insertion on the lattice constant variation has a minimum at $x = 0.20 \pm 0.06$, $\alpha + \beta$ phase, and increases from $x = 0.6$ (β phase).

The normalized resistivity in function of hydrogen content x shows a maximum value of about 1.77 at a concentration of $PdH_{0.76}$.

Acknowledgements

This work has been performed in the framework of cooperation between H.E.R.A. (Hydrogen Energy Research Agency) and FFF (Fondazione Fulvio Frisone). We would like to thank for the help and suggestions our colleagues of WARD (World Association Research and Development) and of INFN-LNF group lead by Dr. Francesco Celani. Special acknowledgements to Italian Republic Senator Dr. Salvo Fleres for his passionate interest in scientific research and to Dr. Sebastiano Truglio for his valuable support. Thanks to our colleagues at TELEDIFE and SEGREDIFESA of Italian Ministry of Defense for their encouragement. Special thanks to our collaborators Jean-Paul Biberian, A. Marmigi, N. Armanet, V. Asarisi, S. Roccasecca and G. Spampinato.

References

[1] P. Tripodi, N. Armanet, V. Asarisi, A. Avveduto, A. Marmigi, J.D. Vinko, J.P. Biberian, Phys. Lett. A 373 (2009) 3101.
[2] P. Tripodi, N. Armanet, V. Asarisi, A. Avveduto, A. Marmigi, J.P. Biberian, J.D. Vinko, Phys. Lett. A 373 (2009) 4301.
[3] F.A. Lewis, K. Kandasamy, X.Q. Tong, Solid State Phenom. 73–75 (2000) 366–422.
[4] F.A. Lewis, K. Kandasamy, X.Q. Tong, Solid State Phenom. 73–75 (2000) 302–365.
[5] T.B. Flanagan, W.A. Oates, Annu. Rev. Mater. Sci. 21 (1991) 269.
[6] J.E. Schirber, B. Morosin, Phys. Rev. B 12 (1975) 117.
[7] A.J. Maeland, T.R.P. Gibb Jr., J. Phys. Chem. 65 (1961) 1270.
[8] D.H. Everett, P.A. Sermon, Zeitschrift fur Phyikalische Chemie Neue Folge 114 (1979) 101.
[9] S.D. Axelrod, A.C. Makrides, J. Phys. Chem. 68 (1964) 2154.
[10] H Numata, I. Ohno, Fusion Technol. 38 (2000) 206.
[11] N. Tsukuda, K. Itoh, N. Morioka, H. Ohkubo, E. Kuramoto, J. Alloys Compd. 293 (1999) 174.
[12] B. Baranowski, F.A. Lewis, W.D. McFall, S.M. Filipek, T.C. Witherspoon, Proc. Roy. Soc. Lond. A 386 (1983) 309.
[13] E. Wicke, G.H. Nernst, Ber. Bunsenges. Phys. Chem. 68 (1964) 224.
[14] Paolo Tripodi, Daniele Di Gioacchino, Jenny Darja Vinko, Braz. J. Phys. 34 (3B) (2004) 1177.
[15] P. Tripodi, M.C.H. McKubre, F.L. Tanzella, P.A. Honnor, D. Di Gioacchino, F. Celani, V. Violante, Phys. Lett. 276A (2000) 122.
[16] Paolo Tripodi, Daniele Di Gioacchino, Jenny Darja Vinko, J. Alloys Compd. 486 (2009) 55.
[17] C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 2005.