



Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla



The effect of hydrogenation/dehydrogenation cycles on palladium physical properties

Paolo Tripodi^{a,b,*}, Nicolas Armanet^a, Vincenzo Asarisi^c, Alessandro Avveduto^c, Alessandro Marmigi^a, Jenny Darja Vinko^a, Jean-Paul Biberian^d

^a H.E.R.A., Hydrogen Energy Research Agency, Corso della Repubblica 448, 00049 Velletri, Italy

^b University of Rome "Tor Vergata", Physics Department, Via della Ricerca Scientifica 1, 00133 Rome, Italy

^c Fondazione Fulvio Frisone, Via Etna 73, 95124 Catania, Italy

^d CNRS, Aix-Marseille Université, CINAM-UPR3118, Campus de Luminy, 13288 Marseille cedex 09, France

ARTICLE INFO

Article history:

Received 24 January 2009

Received in revised form 26 June 2009

Accepted 29 June 2009

Available online 3 July 2009

Communicated by A.R. Bishop

Keywords:

Palladium wire
Hydrogen cycles
Electrolysis
Resistivity
Stress
Strain

ABSTRACT

A series of hydrogenation/dehydrogenation cycles have been performed on palladium wire samples, stressed by a constant mechanical tension, in order to investigate the changes in electrical and mechanical properties. A large increase of palladium electrical resistivity has been reported due to the combined effects of the production of defects linked to hydrogen insertion into the host lattice and the stress applied to the sample. An increase of the palladium sample strain due to hydrogenation/dehydrogenation cycles in $\alpha \rightarrow \beta \rightarrow \alpha$ phase transitions is observed compared to the sample subjected to mechanical tension only. The loss of initial metallurgical properties of the sample occurs already after the first hydrogen cycle, i.e. a displacement from the initial metallic behavior (increase of the resistivity and decrease of thermal coefficient of resistivity) to a worse one occurs already after the first hydrogen cycle. A linear correlation between palladium resistivity and strain, according to Matthiessen's rule, has been found.

© 2009 Elsevier B.V. All rights reserved.

0. Introduction

Studies on palladium–hydrogen (Pd–H) have began in the 19th century [1] and widely investigated since 1960 [2–6]. Hydrogen (H) and its isotopes dissolve in palladium (Pd) occupying interstitial sites in the host lattice, producing an expansion of the lattice [5]. As it is well known, cycles of Pd hydrogenation and dehydrogenation give rise to a series of changes in physical properties of Pd [2]. In particular, H inside the Pd creates displacements of Pd atoms from the original sites and even vacancies which affect the mechanical and electrical characteristics of the Pd sample [3,7]. Since 1990, many efforts have been done to understand the variations of these properties due to the hydrogenation of the metal. It was observed that H produces an increase of the concentration of vacancies inside metals, especially Pd [8–10], by several orders of magnitude compared to vacancies generated by thermal cycles like high temperature annealing [11]. A significant increase in the strain rate (a factor of 6) was observed upon switching from pure Ar

to pure H₂ atmosphere [12]. This is in accordance with statistical mechanics studies on vacancy–interstitial interactions, which predict a significant increase in vacancy concentration. Moreover, high temperature exposure of Pd to H₂ gas atmosphere strongly affects the creep rate [12]. Moreover, cycles of hydrogenation and dehydrogenation in $\alpha \rightarrow \beta \rightarrow \alpha$ phase transition increase the hardness of Pd samples and decrease its ductility [13]. These phase transitions also cause increase in dislocation density [14] and trapping efficiency with respect to H isotopes inside the host lattice [15]. A different behavior of Pd–Pt alloys phase diagrams after hydrogenation/dehydrogenation cycles was observed [16] suggesting a change of H solubility inside the sample.

In this letter, we study the effect of hydrogenation/dehydrogenation cycles (disequilibrium condition) on the physical properties of palladium under stress by constant tension, as well as the effect of the hydrogen cycles on the relative elongation of palladium wires.

With respect to the variation of electrical properties of palladium under stress, it is observed that the electrical resistivity increases after each cycle. Moreover, a residual strain due to the combined effect of hydrogenation and mechanical stress is observed. A linear correlation between the residual length and the electrical resistivity after each cycle is observed probably because

* Corresponding author at: H.E.R.A. Corso della Repubblica 448, 00049 Velletri, Italy. Tel.: +393927868142; fax: +390697258656.

E-mail address: paolotripodi@heraphysics.it (P. Tripodi).

the concentration of defects increases linearly with strain. The kind of internal stress created and in which way it affects the electrical properties of the metal will be discussed.

1. Experimental set-up

Hydrogen is loaded electrochemically inside the Pd lattice using it as cathode and platinum as anode. The electrochemical cell is composed of two long parallel electrodes 5.5 cm apart. In Fig. 1, the scheme of the experimental set-up is shown, where “T” represents the applied tension to the Pd wire ($T \approx 0.49$ N for samples A, B, D, except for sample C where $T \approx 0.28$ N), “a” is the Pd cathode, “b” are the electrical connectors, coated with PTFE tape,

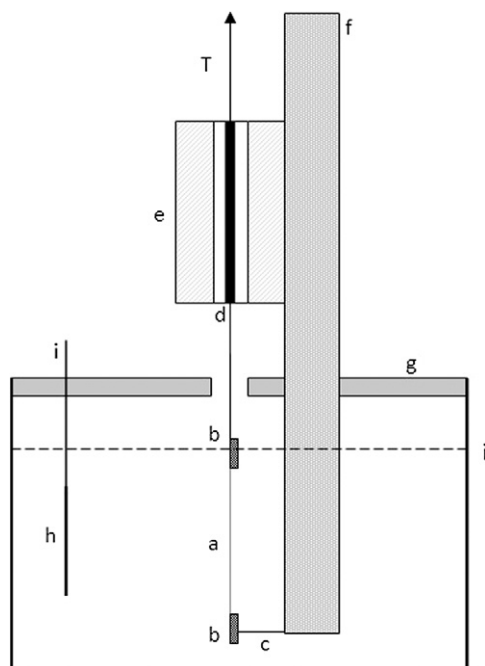


Fig. 1. Experimental set-up: electrolytic cell; scheme of the linear tension–position transducer LVDT; set-up used to maintain in vertical position the palladium wire with a constant tension applied.

used for ac electrical resistance measurement, “c” is a PTFE coated 1 mm in diameter and 1 cm long Pt rod used to connect electrically the lower part of the cathode, “d” is the magnetic probe of the LVDT (Linear Variable Differential Transducer) represented in dark black, “e” is the LVDT transducer, “f” is a PTFE thick cylinder used as sample holder, “g” is in a Plexiglas top, “h” is the Pt anode, “i” is the electrical contact (the part inside the electrolyte is coated with PTFE) and “j” is the electrolyte level.

All parts in contact with the solution are thoroughly coated with PTFE tape, except the cathode and the anode.

The electrolytic cell consists of a 2 litres glass beaker (130×185 mm). The cathodes used for all the experiments were Pd wires of the same batch at 99.9% purity grade (Goodfellow), as received (as drawn), 50 μm in diameter and 8 cm long. The anode was a Pt rod at 99.995% purity grade (Goodfellow) 1 mm in diameter and 6.5 cm long. The experiments are conducted in controlled environment at room temperature, typically 293 K.

The electrolyte, CaSO_4 anhydrous, general purpose grade (Fisher Scientific) at 1.48×10^{-3} M is made with ultra pure water more than $18 \text{ M}\Omega \text{ cm}$, purified by the system “Elix-5/Milli-Q” (Millipore).

Hydrogenation and dehydrogenation consists of cycles of cathodic H loading into Pd cathode (10 Volts) and anodic H unloading from Pd anode (3 Volts) at constant voltage, with no reference electrodes involved. The dc electrolytic current is measured through a shunt resistance $R = 201 \pm 1 \text{ m}\Omega$. Hydrogenation current is 15 mA and dehydrogenation current is 6 mA, corresponding respectively to current densities of about 119 mA cm^{-2} and about 48 mA cm^{-2} .

The 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 (Agilent 4263B) as shown in Fig. 2. The high impedance of the solution avoids parasitic effect on the electrical resistance measurement of the Pd wire. The large distance between electrodes is used to limit possible interference on cathodic chemical reactions.

The elongation of the wire during loadings and its contraction during deloadings are measured during electrolysis. The Pd wire is maintained in a vertical position by a constant tension (Fig. 1). Indirectly linked to this wire, outside of the cell, a LVDT (Solartron Metrology) monitors the variation of the wire length with an error of $\pm 1 \mu\text{m}$ (where $\Delta V = 1 \text{ mV}$ corresponds to $\Delta l = 1 \mu\text{m}$).

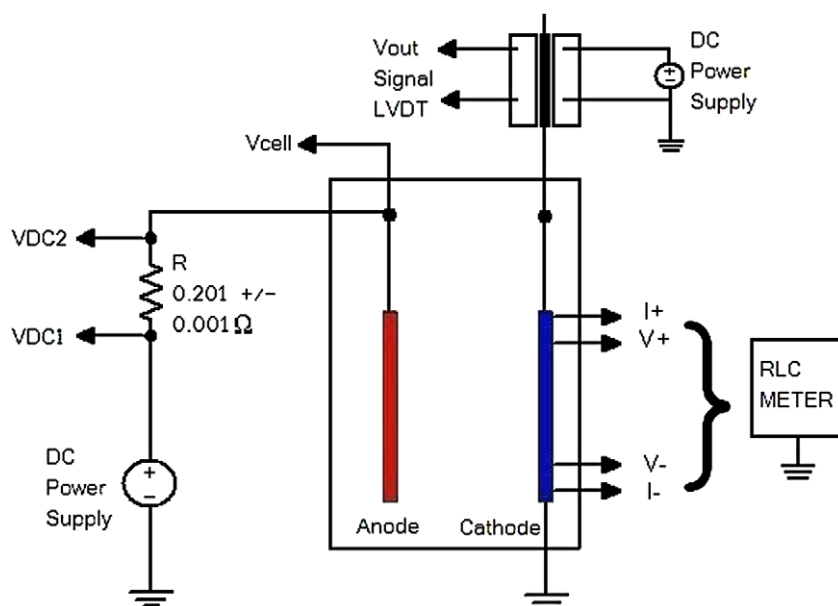


Fig. 2. Electrical scheme of the experimental set-up.

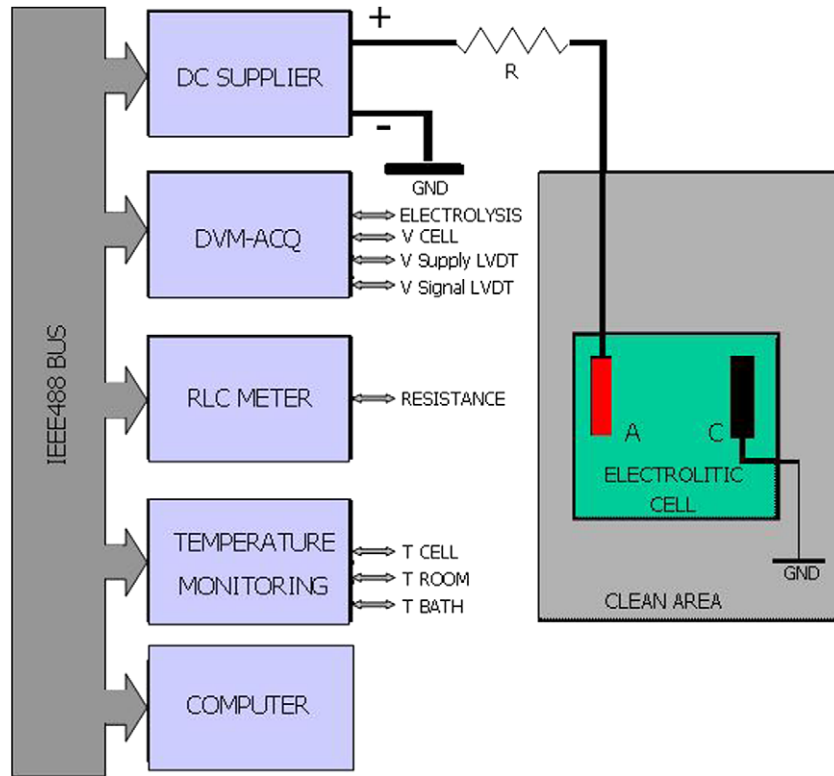


Fig. 3. Global block diagram of the experimental set-up.

The temperature coefficient of resistivity λ is calculated through the measurement of the electrical resistance of the Pd wire at two different temperatures. The electrical resistance measurement of the Pd wire was performed at 293.15 ± 0.01 K and at 353.15 ± 0.01 K by positioning the sample holder from one vessel to another one at these temperatures.

The experimental setup is schematically described in the block diagram shown in Fig. 3. All the instruments are linked to the computer through a GPIB/USB-B (Agilent 82357A) interface and IEEE488 bus.

A constant electrolysis voltage is applied by a DC power supplier (Agilent 6035A) with a precision of 10 mV. All voltage parameters are acquired using a data acquisition system (Agilent DVM 34970A) at a sampling rate of 1 Hz, the ac electrical resistance is measured with a RLC meter (Agilent 4263B), with a precision of 20 m Ω and the temperatures are measured by PT100 sensors connected to a temperature monitor (Lake-Shore 218) with a precision of 0.01 K.

2. Results

The objective of these experiments is to study the effect of hydrogenation and dehydrogenation cycles on the strain ε ($\varepsilon = \Delta l/l$) and the electrical resistivity of Pd at constant tension applied. The cycles consist in H loading in Pd cathode and subsequent H deloading from it. The experiments are performed with the Pd wire described in the experimental section, stressed by a constant tension $T \approx 0.49$ N, equivalent to an initial pressure of about 260 MPa. Seven cycles of hydrogenation/dehydrogenation were performed before rupture of the wire.

Fig. 4 shows the Pd wire (sample A) resistance measurements and the relative length variation v.s. time during the first three cycles. Before each new cycle, the resistance thermal coefficient is measured as described in the previous section. The H loading inside Pd wire is obtained by potentiostatic condition (10 Volts).

We observe, as expected, that the introduction of hydrogen into the lattice causes the increase of the Pd resistance [3], and the expansion of the Pd lattice [5].

On the contrary, applying a reverse difference of potential of 3 V we obtain the dehydrogenation of the Pd wire, and decrease of the Pd wire resistance and length.

After each cycle we observe a residual elongation of the wire, as well as an increase of $R_{0,n}$, which suggests a progressive internal stress of the Pd sample. $R_{0,n}$ represents the resistance of Pd wire with no hydrogen inside the lattice (the first index “0”) at the end of the corresponding dehydrogenation cycle (the second index “n”).

This behaviour is shown in Fig. 5, where the strain $\varepsilon = \frac{\Delta l}{l_{0,0}}$ and the resistance of the Pd wire (sample A) after each cycle with no H inside the lattice is plotted.

The initial length $l_{0,0}$ is estimated by the well-known relationship (1):

$$l_{0,0} = \frac{R_{0,0} \cdot S_{0,0}}{\rho_{0,0}} \quad (1)$$

where $R_{0,0}$ is the resistance of the Pd wire before starting the experiment, $S_{0,0} = (19.25 \pm 0.12) \times 10^{-6}$ cm² is the initial Pd wire cross section obtained by SEM (Jeol-JSM-6320F) analysis, as described below, and $\rho_{0,0} = 10.54 \pm 0.01$ $\mu\Omega$ cm is the resistivity of pure Pd [17] at the temperature of the experiment. In these conditions we obtain an initial $l_{0,0} = 7.94 \pm 0.08$ cm (sample A).

The values of length at the end of each cycle are calculated considering the Δl variation (measured by LVDT) with respect to the initial value $l_{0,0}$. After six cycles, the Pd wire length increases by about 0.7 cm, which corresponds to an elongation percentage $\varepsilon = 8.7\%$ (Fig. 5).

In Fig. 6, values of initial resistance $R_{0,n}$ are plotted as a function of the initial length $l_{0,n}$ of each cycle (data in Fig. 5), with the corresponding fit. The behaviour of this function is linear with a very high correlation coefficient. From this data it's possible to evaluate the ratio between the resistivity $\rho_{0,n}$ and the

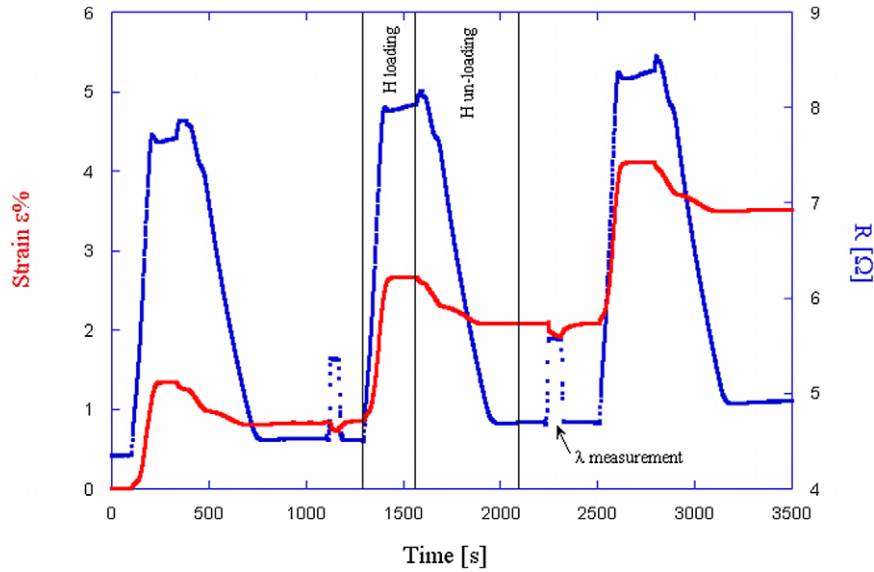


Fig. 4. Strain (red) and Resistance (blue) of the palladium wire versus time (sample A). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

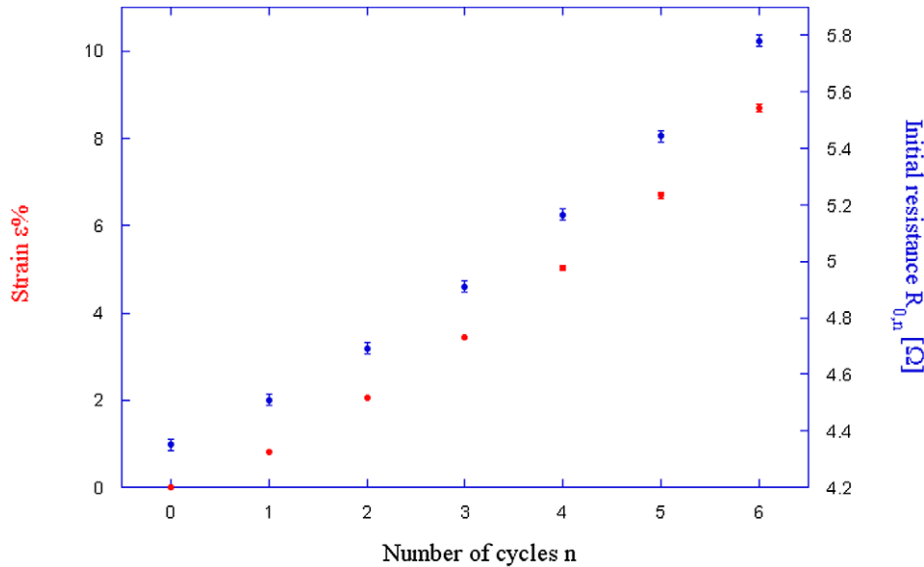


Fig. 5. Strain and initial resistance of Pd wire, after each cycle (sample A).

cross section $S_{0,n}$ of the palladium sample, by using the relationship (2):

$$\frac{\rho_{0,n}}{S_{0,n}} = \frac{R_{0,n}}{l_{0,n}}. \quad (2)$$

Should this ratio be constant after each cycle, a curve fit with an intercept to zero should be observed. Since the intercept obtained is not zero, it is clear that the resistivity-section ratio $\rho_{0,n}/S_{0,n}$ changes during the experiment.

To estimate the variation of the resistivity $\rho_{0,n}$ after each cycle we determine the cross section of the Pd wire during the experiment. The cross section is obtained by measuring the Pd wire diameter on an SEM image. Fig. 7 shows the palladium wire after 1 and 7 cycles.

By this measurement it is possible to extrapolate in first order approximation a linear behaviour of the diameter variation after each cycle, as shown in Fig. 8. The effect of hydrogenation/dehydrogenation process with a constant tension applied to the Pd sample,

is to decrease the wire cross section (Fig. 8) while the length increases (Fig. 5). This irreversible change in the dimensions already occurs after the first cycle.

Using the fit of Fig. 8 we can now calculate the behaviour of the resistivity $\rho_{0,n}$ during the experiment.

As shown in Fig. 9 (samples A and B) $\rho_{0,n}$ is a monotonically increasing function versus hydrogenation/dehydrogenation cycles number. Pd resistivity variation of about 15% from its initial value is observed, which is an unexpectedly large variation.

Hydrogenation/dehydrogenation cycles enhance already existing line and local defects increasing the electronic scattering centres [7] that cause the $\rho_{0,n}$ increase.

The palladium sample D has been stressed by mechanical tension without hydrogenation cycles, in order to evaluate the contribution on the defects enhancement caused only by mechanical stress (Fig. 10).

In Fig. 10 the strain $\ln(\varepsilon)$ versus time (strain–time curve) for a virgin Pd wire with an applied tension of $T \approx 0.49$ N (same tension applied to the samples A and B) is plotted.

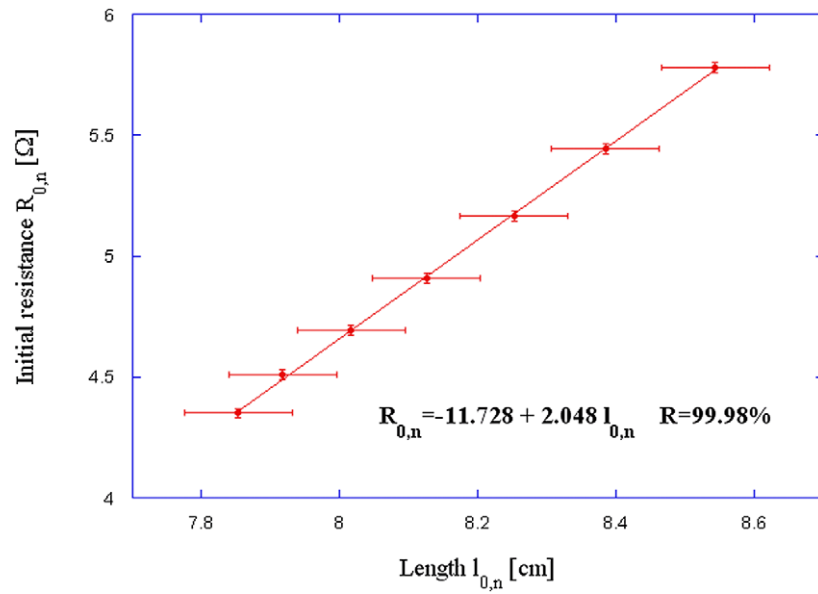


Fig. 6. Initial resistance versus initial length for Pd wire (sample A).

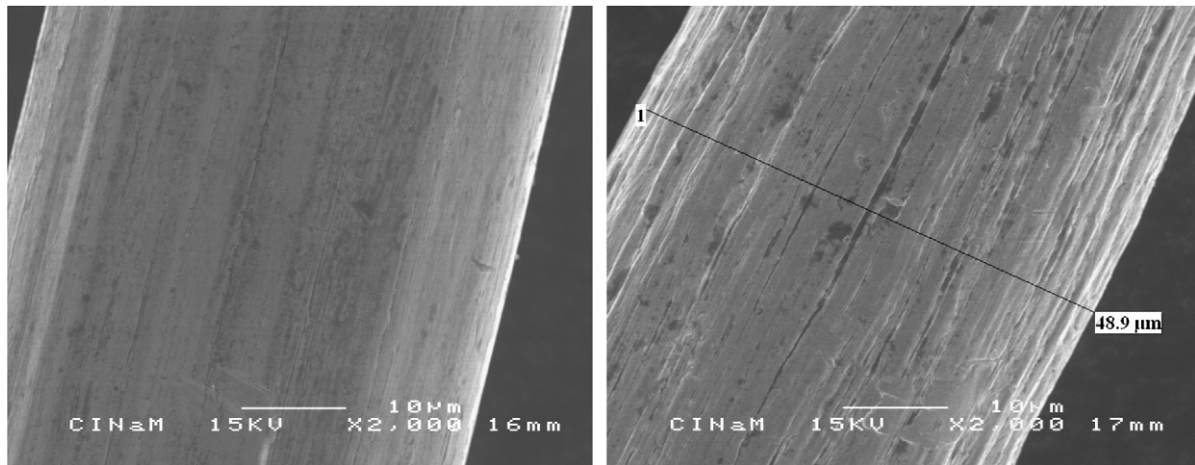


Fig. 7. Pd wire SEM images of cycle 1 and cycle 7.

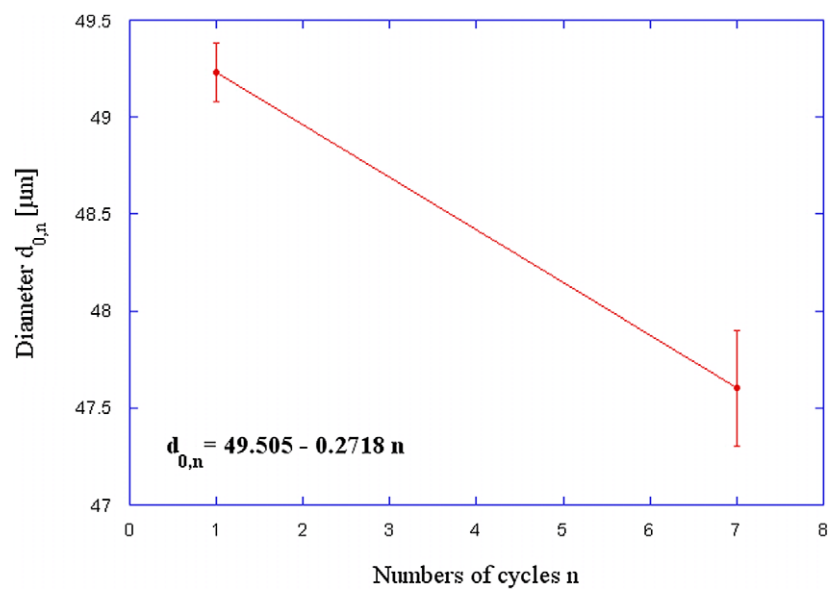


Fig. 8. Pd wire diameter versus the number of cycle: cycle 1 and 7; linear extrapolation of the diameter versus number of cycle.

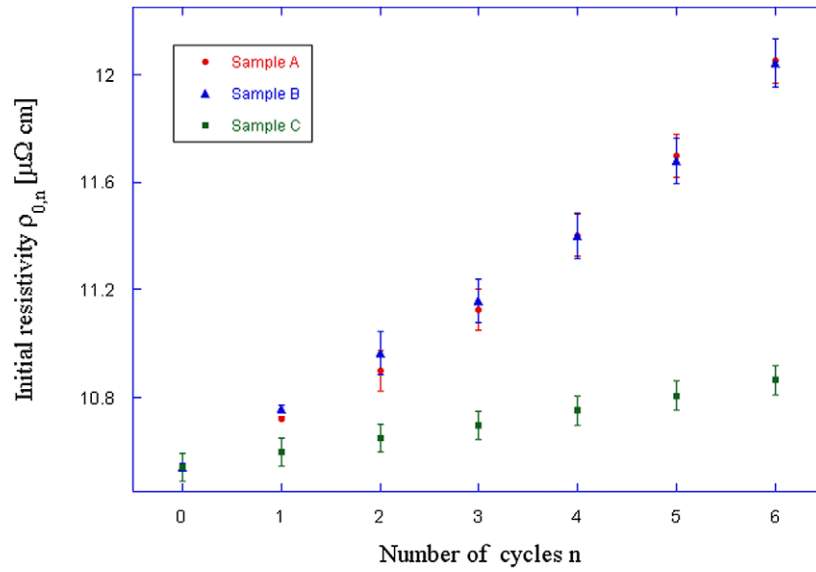


Fig. 9. Initial Pd wire resistivity after each cycle (samples A, B, C).

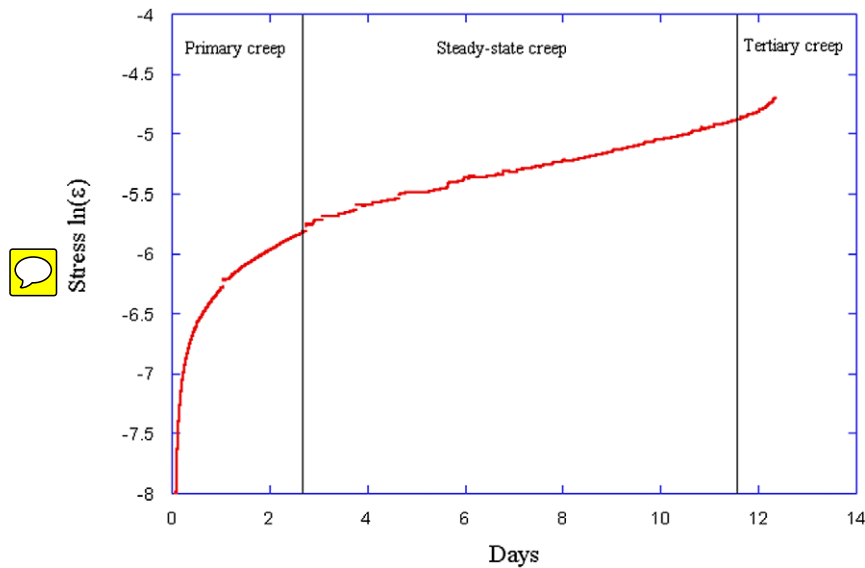


Fig. 10. Logarithm of strain versus time (sample D).

In a strain–time curve, three different regions (primary creep, steady-state creep and tertiary creep) are present. The tertiary creep region ends when the rupture of the wire occurs. During this experiment, all the resistivity results of the Pd sample ($\rho_0 = 10.54 \mu\Omega \text{ cm}$) are inside the error bar of 0.4% in all the three regions.

This means that the effect of the only mechanical stress without H cycles strain is negligible on the Pd sample resistivity compared to the 15% resistivity increase due to H cycles strain (with $T \approx 0.49 \text{ N}$).

Moreover, another important evidence is that the experiment of six H cycles lasting about two hours gives $\varepsilon = 8.7\%$, while the elongation percentage obtained with the single mechanical tension in the corresponding time gives only $\varepsilon = 0.03\%$ (Fig. 10).

In order to understand if, on the contrary, the increase of the Pd resistivity is only due to the effect of hydrogen diffusion inside the host metal and not to the strain, an experiment reducing the applied tension to $T \approx 0.28 \text{ N}$ (sample C) has been performed. In fact Figs. 9 and 11 show that the strain is less pronounced

after each cycle when a lower tension is applied to the Pd (sample C).

We observe that after the same number of H cycles as for samples A and B, the resistivity of sample C (Fig. 9) increases only of about 3%, suggesting a correlation between the variation of the resistivity and the strain of the sample.

By plotting the resistivity values $\rho_{0,n}$ in function of the strain ε (Fig. 11), we observe a linear correlation, where the slope does not depend neither on the number of the cycles nor on the tension applied. We can conclude that the increase of the resistivity is a phenomenon due to the combined effect of mechanical stress and hydrogen disequilibrium inside the metal, where disequilibrium is the H dynamics in the Pd lattice during the H cycles. In fact, at the equilibrium concentration H/Pd inside the Palladium, there is no variation of parameters like resistivity and strain.

The linear dependence of resistivity–strain is in accordance with Matthiessen's rule [18], where the resistivity in a stretched sample is a sum of resistivity resulting from electrons scattering on phonons (ρ_p), deformed lattice (ρ_e) and crystalline defects (ρ_d):

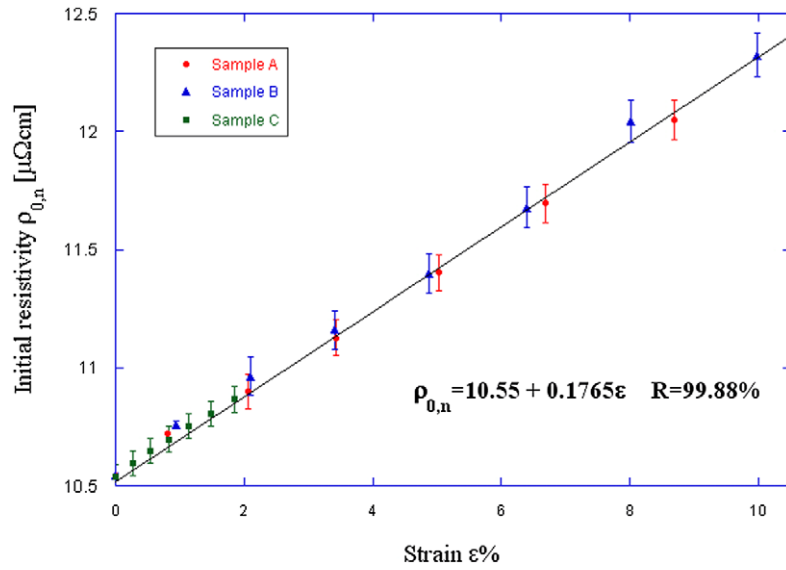


Fig. 11. Initial Pd wire resistivity versus relative elongation (samples A, B, C).

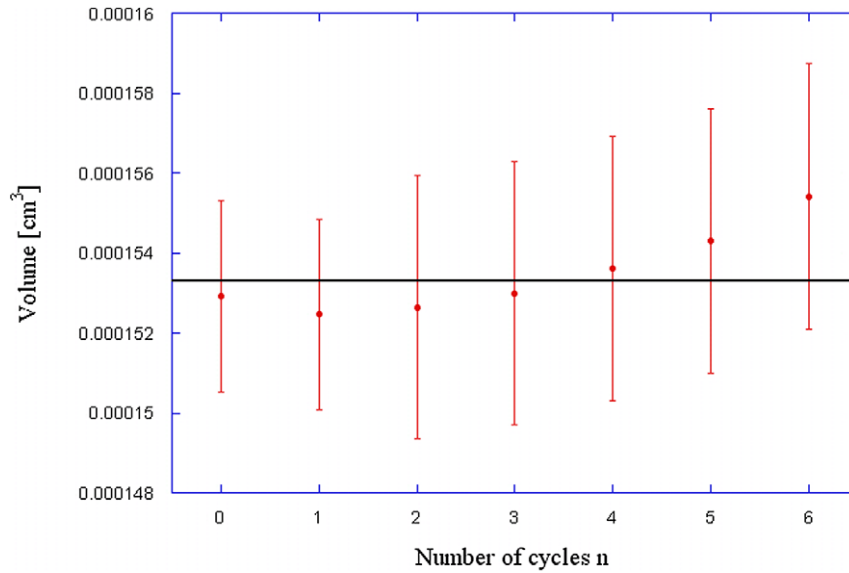


Fig. 12. Pd wire volume after each cycle obtained by the linear extrapolation of the diameter (Fig. 8) and from the length measurements.

$$\rho = \rho_p + \rho_\varepsilon + \rho_d. \quad (3)$$

The resistivity ρ_ε resulting from electrons scattering on a deformed lattice through stretching, is in first approximation proportional to the relative length increase ε :

$$\rho_\varepsilon = k_\varepsilon \cdot \varepsilon \quad (4)$$

and the resistivity ρ_d resulting from the electron scattering on defects is proportional to their concentration C_d :

$$\rho_d = k_d \cdot C_d \quad (5)$$

and that during stretching, new defects occur, where the growth in concentration ΔC_d is proportional to the relative elongation ε :

$$\Delta C_d = k_1 \cdot \varepsilon. \quad (6)$$

Then, in a stretched sample, the relationship describing relative change in resistivity as a function of the relative growth in length is:

$$\frac{\Delta \rho}{\rho_{0,0}} = \frac{\rho_{0,n} - \rho_{0,0}}{\rho_{0,0}} = \left[\frac{k_\varepsilon + k_d \cdot k_1}{\rho_p + k_d \cdot C_0} \right] \cdot \varepsilon = K_H \cdot \varepsilon \quad (7)$$

where k_ε , k_d and k_1 are constant parameters, and C_0 denotes the concentration of defects in the non-stretched sample. Formula (7) is applicable if ρ_p does not change during the cycles. Experimental data show that the constant K_H in the relation (7) is at least one order of magnitude higher than the same constant obtained without the H cycles.

We observe that after each hydrogenation/dehydrogenation cycle, the volume is inside the error bar of about 2% (Fig. 12).

We also investigated the effect of the hydrogenation/dehydrogenation cycles on the thermal coefficient of resistivity λ as shown in Fig. 13. We observe almost a linear decrease of λ after each cycle (deloaded), which is coherent with the increase of the resistivity suggesting a progressive displacement from the initial metallic behaviour of the sample. The total decrease of thermal coefficient of resistivity λ for Pd sample with respect to the initial value is about 4%.

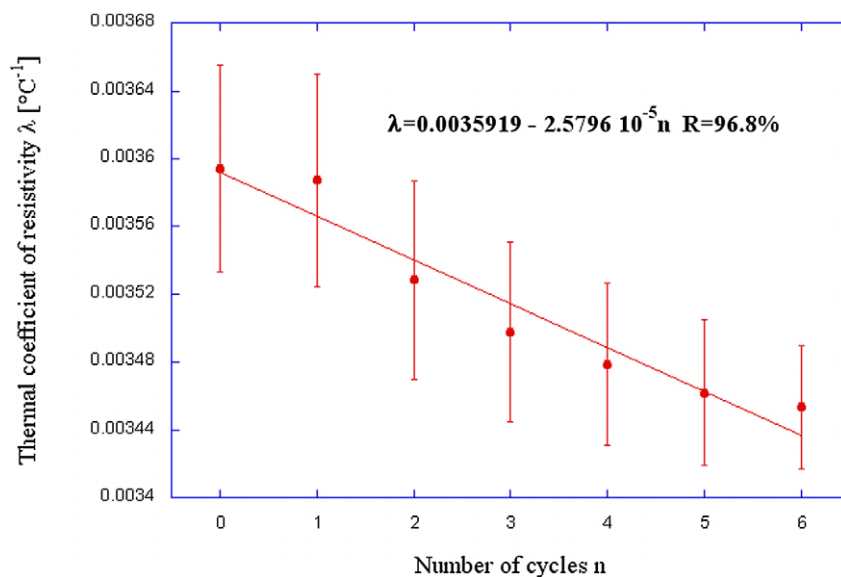


Fig. 13. Thermal coefficient of resistivity versus the number of cycles (sample A).

3. Conclusion

A series of hydrogenation/dehydrogenation cycles produces a large change in resistivity of Pd stressed by a constant tension. This increase of Pd resistivity is mainly due to the defect formation caused by both H insertion and mechanical stress.

These H cycles produce mechanical change (internal stress) inside the Pd lattice. Whatever the initial state condition of the Pd sample, our experimental data suggest that the Pd lattice loses the initial state conditions already following the first H cycle. Particularly, the application of a constant tension to the Pd wire, during the H cycle series, produces a progressive large strain up to 8.7% of its initial length in a very short time span compared to the same sample affected only by constant tension. This large strain is due to the combined effect of mechanical stress and H dynamics in the Pd lattice during H cycles. We can conclude that the hydrogen not only speeds-up the variation of Pd sample strain and resistivity but also increases the entity of these phenomena.

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 suggestion 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 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.

References

- [1] T. Graham, Philos. Trans. R. Soc. London 156 (1866) 399.
- [2] F.A. Lewis, The Palladium Hydrogen System, Academic Press, London, New York, 1967.
- [3] G. Alefeld, J. Völkl, Hydrogen in Metal II, vol. 29, Springer-Verlag, 1978.
- [4] F.A. Lewis, Platinum Metals Rev. 26 (1) (1982) 20.
- [5] F.A. Lewis, Platinum Metals Rev. 26 (2) (1982) 70.
- [6] F.A. Lewis, Platinum Metals Rev. 26 (3) (1982) 121.
- [7] C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 2005.
- [8] I.M. Robertson, Eng. Fracture Mech. 64 (1999) 649.
- [9] Y. Shirai, H. Araki, T. Mori, W. Nakamura, K. Sakaki, J. Alloys Compounds 125 (2001) 330.
- [10] K. Sakaki, T. Yamada, M. Mizuno, H. Araki, Y. Shirai, Mater. Trans. JIM 43 (2002) 2652.
- [11] Yuh Fukai, J. Alloys Compounds 231 (1995) 35.
- [12] G. Majkic, S. Karajagi, U. Balachandran, K. Salama, Mater. Sci. Eng. B 150 (2008) 145.
- [13] G. Jimenez, E. Dillon, R. Miller, F. Massicotte, S. Nesbit, A. Craft, Scr. Materialia 59 (2008) 870.
- [14] G.I. Zhiron, M.V. Goltsova, G.E. Shatalova, Int. J. Hydrogen Energy 31 (2006) 231.
- [15] B.J. Heuser, J.S. King, J. Alloys Compounds 261 (1997) 225.
- [16] H. Noh, T.B. Flanagan, Y. Sakamoto, J. Alloys Compounds 231 (1995) 10.
- [17] CRC Handbook of Chemistry and Physics, 85th edition, 2005.
- [18] R. Pietrzak, R. Szatanik, Physica B 315 (2002) 215.