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Transformation mismatch plasticity in Pd induced by cyclic hydrogen charging

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ABSTRACT

Transformation mismatch plasticity is achieved in swaged palladium wires by cyclical hydriding–dehydriding. Upon multiple cycles at ambient temperature, a total strain of ~40% is accumulated under a constant tensile stress. This value is much higher than the tensile ductility for swaged Pd subjected to monotonic deformation without transformation (<2% for this wire). Strain increments after a single cycle are proportional to the applied stress, in agreement with the Greenwood–Johnson equation for transformation mismatch plasticity. The yield stress of hydrogen-cycled Pd calculated from this equation is 760 MPa, which is much higher than the value of the original wire and about 50% higher than previous values reported for Pd that was hydrogen cycled at 100 °C without an applied stress.

1. Introduction

Transformation mismatch plasticity can be induced in allotropic material by subjecting them to an applied stress during a phase transformation. Internal strains produced by the mismatch between the two coexisting allotropic phases are biased in the direction of the external stress, resulting in a strain increment after each transformation which is proportional to the biasing stress at low stresses. Strain increments created during cyclical transformation can be accumulated into large macroscopic strain (<100% in tension), a phenomenon called transformation superplasticity [1–3]. The phase transformation can results from thermal cycling in various metals and alloys [3–9] and has also been recently achieved by chemical cycling in titanium, i.e., by repeated hydrogen charging/discharging cycles under isothermal conditions [10,11]. In the latter case, additional internal mismatch due to lattice swelling can be generated by hydrogen gradient within the sample without transformation, which can also produce strain under biasing by an applied stress [12].

Hydrogen-induced transformation mismatch plasticity has been studied exclusively in titanium and titanium alloys [2,10–15] at elevated temperature, where the diffusion of hydrogen in and out the sample is rapid. Palladium is unique among metals, as it exhibits, at ambient temperature, high solubility and diffusivity for hydrogen [16–19]. Hydrogen dissociation on the Pd surface is highly not sensitive to "poisoned" due to exposure to air or humidity [19]. At ambient temperature, the equilibrium absorption and desorption pressure of H_2 in Pd are ~2.5 and 1.3 kPa, respectively [19,20] and the hydrogen to palladium ratios (H/Pd) in saturated Pd and in the hydride are ~0.015 and 0.6, respectively. At partial pressure of 100 kPa H_2 (~1 atm) the H/Pd ratio is reaching ~0.7, resulting in lattice swelling of about 10% [17]. Upon heating to about 150 °C, the hydrogen desorption pressure is ~100 kPa.

The mechanical properties of Pd and Pd alloys have been studied by various authors (see for example Ref. [21]). However, relatively little is known about the mechanical properties of Pd–H alloys [22]. The Pd mechanical properties after hydriding–dehydriding cycles have been studied by Goltsov et al. [23–28] and by Goods and Guthri [22]. It was found that hydriding–dehydriding cycles increased the yield and tensile strength of Pd after as few as 1–2 cycles, boosting strength by a factors 2–4 with respect to the initial strength [28], but decreasing uniform elongation to value of less than 3% [22]. This strengthening effect was named HPN (hydrogen phase "naklep") by Goltsov [23]. Additionally, Goltsov demonstrated that plastic deformation of Pd wire (90%) followed by hydrogen cycling at 100 °C can lead to transformation induced plasticity (TRIP), increasing of the total strain of cold-worked Pd from ~5% to ~25% [29], close to the value achieved for annealed sample [21,22,29]. This treatment combining plastic deformation and hydrogen cycling also increases the yield strength of the sample to values of 450–500 MPa [29].

Here, we demonstrate for the first time that Pd can be deformed by hydrogen-induced transformation mismatch plasticity through hydrogen cycling under a constant applied stress at near ambient temperature.

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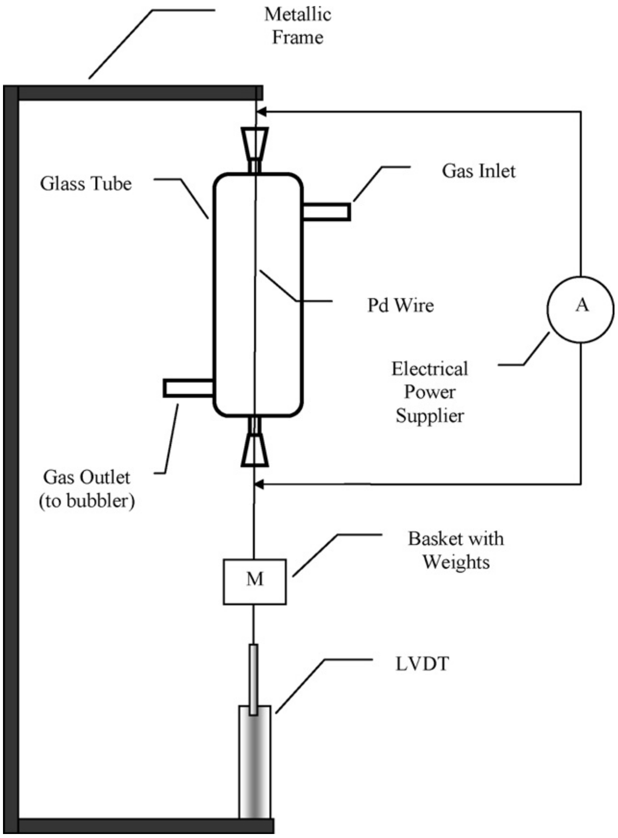

Fig. 1. Schematic of experimental apparatus.

2. Experimental procedures

A schematic of the experimental apparatus is shown in Fig. 1. A 0.25 mm diameter Pd wire (99.99% purity from Alfa Aesar) was used in its as-received condition; the wire was not annealed as it is known [22] that swaged palladium that was annealed recovers its swaged mechanical properties already after 1–2 hydriding/dehydriding cycles. The wire was subjected to uniaxial tension through dead-loading using a basket with weights. The wire deformation was measured by a linear variable differential transducer (LVDT). A 120 mm length of the Pd wire (about half the total length) was threaded through a glass tube with narrow openings (~0.5 mm diameter) without additional sealing. The tube had gas inlet and outlet, allowing atmosphere changing within the tube by dynamic flow of different gasses. The gas outlet connected to a bubbler filled with oil. The whole system was placed in a hood for safety purpose.

The gases used were pure hydrogen and pure argon by dynamic flow, and air by natural flow (allowing the tube atmosphere to be changed by the natural gas flow through the small space between the wire and the tube openings). When dynamic gas flow was used, the bubbling rate was fixed to 1–2 bubbles per second. This arrangement ensures that the total gas pressure within the glass tube was always somewhat higher than ambient pressure (about 1 atm). Hydrogen absorption was always performed at room temperature by dynamic flow of 99.999% pure hydrogen. Full absorption was achieved within about 4 h, as determined by the end of wire elongation. Desorption was done in air at room temperature over a time span of a few days, followed in some cases by a few hours at a somewhat elevated temperature reached by Joule heating of the wire (1.0–1.5 A current) using a stabilized electrical power supplier. The wire temperature was not measured, but since the wire did not glow and the glass tube did not warm, it is assumed that the wire temperature during heating is in the range 100–300 °C. In few cases, the hydrogen desorption occurred in 99.999% pure argon by dynamic flow at room temperature, but the desorption rate was found to be much slower than in air. Full desorption in air at room temperature took from ~36 h to ~2 weeks, while at elevated temperature the maximum desorption time was shortened to ~2 days.

When a dynamic gas flow is used, the total pressure is practically equal to the hydrogen or argon partial pressure (about 1 atm), but when natural gas flow is used (desorption in air) the total pressure is the sum of the air pressure entering the tube and the hydrogen pressure desorbing from the Pd wire. Since the hydrogen is lighter than air, and the desorption rate is relatively slow (see Section 3), it is assumed that the hydrogen partial pressure at this stage is negligible.

The wire strain was calculated under the assumption that the only section of the wire undergoing composition change corresponds to the length, $L_0 = 120$ mm, within the glass tube, as the system is placed within a hood and hydrogen gas escaping through the narrow glass tube upper and lower openings is immediately removed. The engineering strain was calculated as $\varepsilon = \Delta L/L_0$, with ΔL as the elongation of the wire measured by the LVDT. The true strain and the engineering strain are in this case equal, since the actual length of the wire subjected to chemical cycling, and thus deformation, remains constant. The true stress, calculated under the assumption of volume conservation, was in the range 20–200 MPa.

For comparison, three as-received wires were tensile tested using grips designed especially for wires. The gauge length was 120 mm (same as in the hydrogen cycling experiments) and the strain rate was 8.3×10^{-3} min^{-1} (cross-head speed of 1 mm/min). The wires fractured between the grips after some necking, with a total elongation of only 1.7 ± 0.3%. The yield and ultimate tensile stress are 350 ± 20 and 415 ± 5 MPa, respectively.

3. Results and discussion

3.1. Strain history during transformation mismatch plasticity experiments

The strain vs. time plot for an experiment performed at room temperature under variable stress is shown in Fig. 2. The experiment was started at a relatively low stress of ~40 MPa. The first hydriding half cycle (Region A in Fig. 2) results in a strain of 2.8%, in good agreement with the value reported for lattice expansion dur-

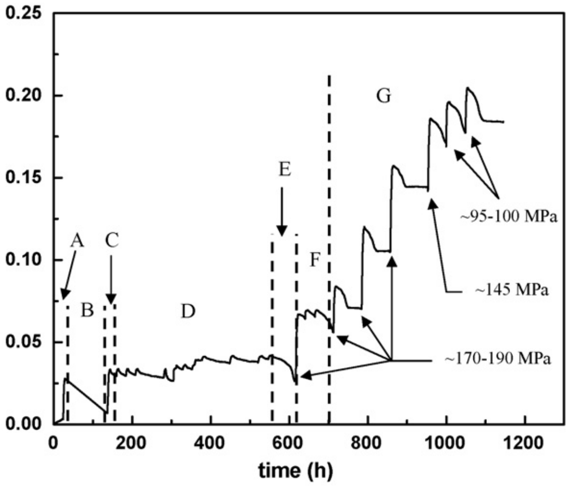

Fig. 2. Plot of strain vs. time for an experiment performed at room temperature under variable stress. Details are given in the text.

ing hydrogenation [17]. Upon desorption for ~100 h in air (B), the wire shrunk by 2.0% thus accumulating 0.8% after this first cycle. The second hydriding half cycle resulted in a strain increment of 2.4% (C). The next few cycles were carried out under argon for the dehydriding half cycles, which did not result in successful desorption (D) and very little strain change, despite a gradual increase in stress to 120 MPa. Subsequently, the desorption atmosphere was changed to air, resulting in a strain decrement of 1.2% (E). This behavior is attributed to the need of oxygen, and possibly some humidity, to catalyze the hydrogen atoms recombination on the metal surface [30]. Further cycling experiments were conducted at various stresses (F and G) between 95 and 190 MPa, with strain increments of up to 3.7% after a complete hydriding–dehydriding cycle. It is evident that desorption time of about 24 h is not long enough to achieve full desorption (F), and should be at least 36 h (G). After reaching ~20% total strain, the experiment was terminated without wire fracture.

Performing a similar experiment under an even lower stress of ~20 MPa (Fig. 3) resulted in the same qualitative behavior: expansion during absorption under pure hydrogen and contraction during desorption in air; however a negative strain increment (i.e., a shortening of the wire) was accumulated at the end of each cycle. This is indicative of negative ratcheting, which can occur under zero applied stress and seems to not have been overcome by the low stress of 20 MPa. Fig. 3 also illustrates the trend of the reaction kinetics. The first dehydriding half cycle (D1) takes longer than the next one (D2). This so-called activation phenomenon is well known in metal–hydrogen reaction [16]. However, the length of the subsequent dehydriding half cycles increases again, with the last one (D5) taking ~2 days (for much longer experiment the desorption half cycle takes up to ~2 weeks, see Fig. 4). We attribute this phenomenon to the formation of dislocations and other lattice defects within the metal, which act as trapping sites for the hydrogen and hence reduce its effective desorption pressure and lower the dehydriding kinetics, as previously observed [23]. The shape of each cycle reveals the different stages of the reaction, as illustrated in Fig. 3 for cycle 4. During the hydriding half cycle (H4), the rapid strain increase (a) can be attributed to the metal → hydride phase transformation, and it is followed by a stage (b) with slower strain changes, due hydrogen dissolution in the hydride. Conversely, during the dehydriding half cycle (D4), a slow decrease of the strain (c) occurs during the hydrogen desorption from the hydride, followed by a rapid strain decrease (d) during the hydride → metal phase transformation, followed again by a slow strain decrease (e) due to hydrogen desorption from the metal.

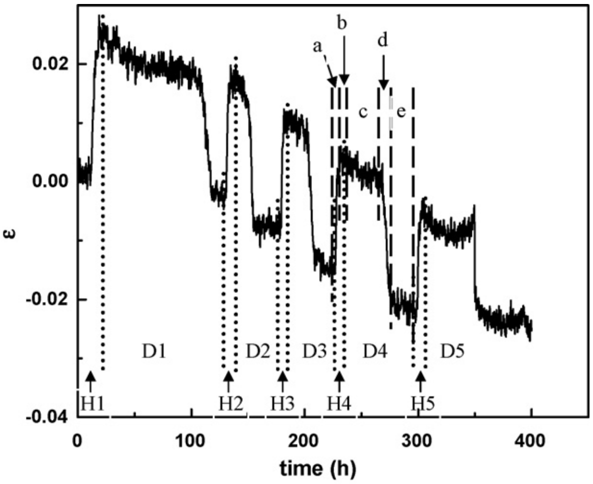

Fig. 3. Plot of strain vs. time for an experiment performed under low stress (~20 MPa) at room temperature. Hydriding and dehydriding (in air) half cycles are delineated by vertical dotted lines and labeled H and D, respectively. Additional details are given in the text.

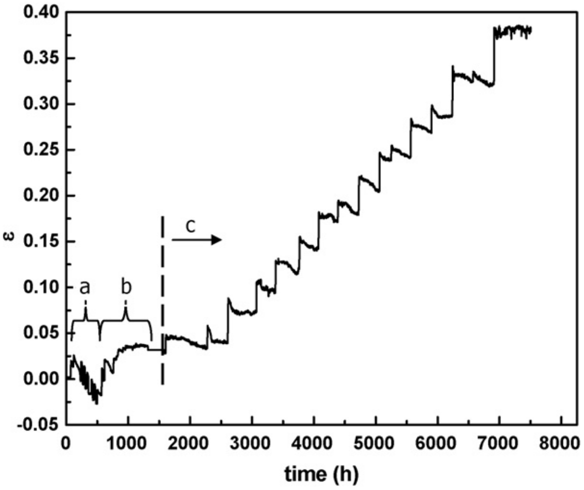

Fig. 4. Plot of strain vs. time for a long-term experiment performed at room temperature. At first ($t < 500$ h) the stress is low (~20 MPa) (region a), it is then increased gradually (region b), and beyond ~1500 h the stress is maintained in the range 160–175 MPa (region c).

A long-term experiment (lasting almost one year) is shown in Fig. 4. The initial stress was ~20 MPa, as in the experiment reported in Fig. 3, and the same phenomena can be seen. After the first few cycles at ~20 MPa (a), the stress was gradually increased (b) and then a series of cycles were performed under a stress ~160–175 MPa (c). Since the desorption time became very long, full desorption was not achieved in a few cases before the onset of the next absorption half cycle, resulting in a reduced extension during the following absorption cycle. When full desorption was achieved, the next hydriding half cycle usually resulted in strain increase of 4–5%. The experiment was terminated after a total strain of almost 40% was accumulated. This value is unusually high, given the following points. First, this strain was achieved without fracture. Second, the wire initial condition was swaged, which usually results in <5% tensile ductility [21,22,29] (a value of <2% was measured for the present wire). Third, when a 90% cold-worked Pd wire is subjected to hydriding–dehydriding cycles at 100 °C without stress, and then tensile tested at room temperature, the tensile ductility is only ~25% [23], Finally, the 40% ductility is slightly higher than the value usually achieved with annealed Pd [21,22,29]. This unusually high tensile ductility is attributed to the well established observation that metals deforming by transformation mismatch plasticity have excellent resistance against flow instability (necking and cavitation) [1,2,13].

In two subsequent experiments, the duration of the desorption half cycle was reduced to <3 days by Joule heating, while the absorption half cycle was unchanged at ambient temperature. In the first experiment, a constant stress of ~125 MPa was maintained during both hydriding and dehydriding half cycles, while in the second, the stress was high (~90 MPa) during the hydriding half cycle and much reduced (~20 MPa) during the dehydriding half cycle. In both cases, the wire reached only ~17% strain before fracturing during a heating dehydriding half cycle. It is assumed that necks that formed during deformation (see Figs. 5–7) were subjected to local overheating due to the Joule heating method used here, leading to failure.

3.2. Microstructure

SEM pictures of the as-received and deformed wires are shown in Figs. 5–7. The as-received wire (Fig. 5a–c) has a relatively smooth surface (with some markings from the wire drawing operation) and

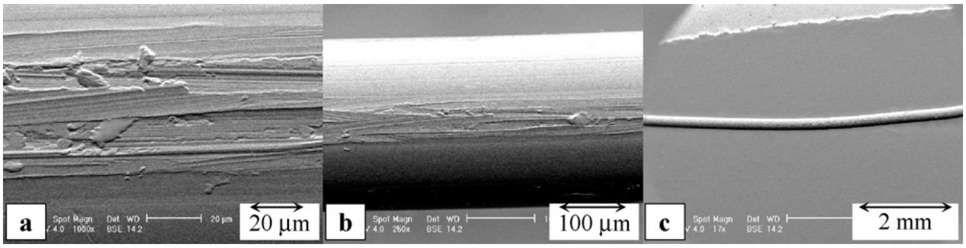

Fig. 5. SEM micrograph showing topographic contrast of as-received wire. (a–c) Side views of wire.

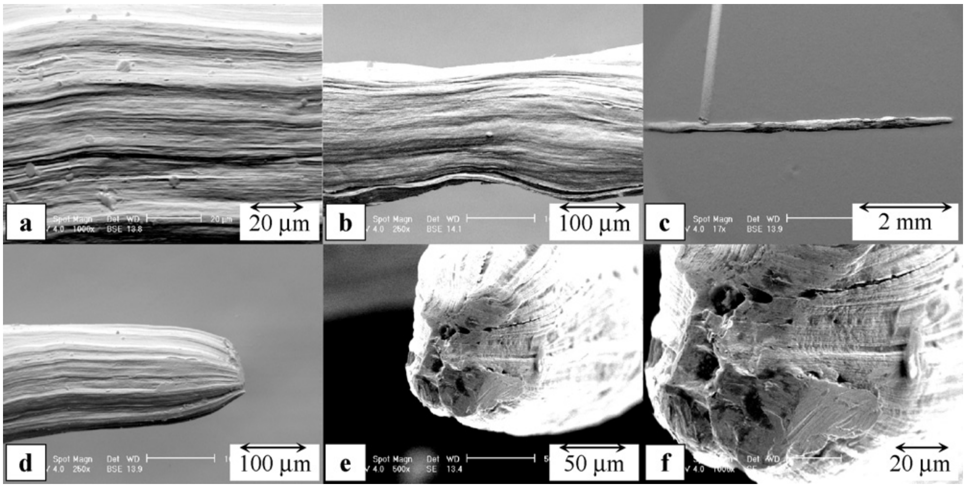

Fig. 6. SEM micrograph showing topographic contrast of wire which reached ~40% strain after experiment at room temperature. (a–c) Side view far from the fracture site; (d) side view of fracture site; (e and f) top view of fracture surface.

shows a uniform cross section with a circular shape. By contrast, the surface of the wire, whose strain history is shown in Fig. 4, has many furrows after a strain of ~40%, and its cross section is distorted and far from being circular (Fig. 6a–c). The average diameter of the strained wire is about 200 μm, which corresponds to ~36% reduction of area. This value is in good agreement with the value of ~33% calculated using volume conservation. The structure of the wire which was Joule heated and reached ~17% strain (Fig. 7a–c) is intermediate between those of the as-received wire and the highly deformed one. The fractured surface of the unheated wire (Fig. 6d–f) is almost perpendicular to the wire axis and its diameter is about 100 μm, which corresponds to $R_A \approx 85\%$ (this wire fractured due to an external mechanical stress, not because of the cycles), while the heated wire (Fig. 7d–f) shows necking to a point, corresponding to $R_A \rightarrow 100\%$.

3.3. *Effect of stress on strain per cycle*

Two plots of strain increment vs. applied stress are shown in Figs. 8a and b: the first is for strain accumulated after one hydriding half cycle, $\Delta\varepsilon_{\text{half cycle}}$ (Fig. 8a) and the second is for the strain accumulated after a full hydriding–dehydriding cycle, $\Delta\varepsilon_{\text{tot}}$ (Fig. 8b).

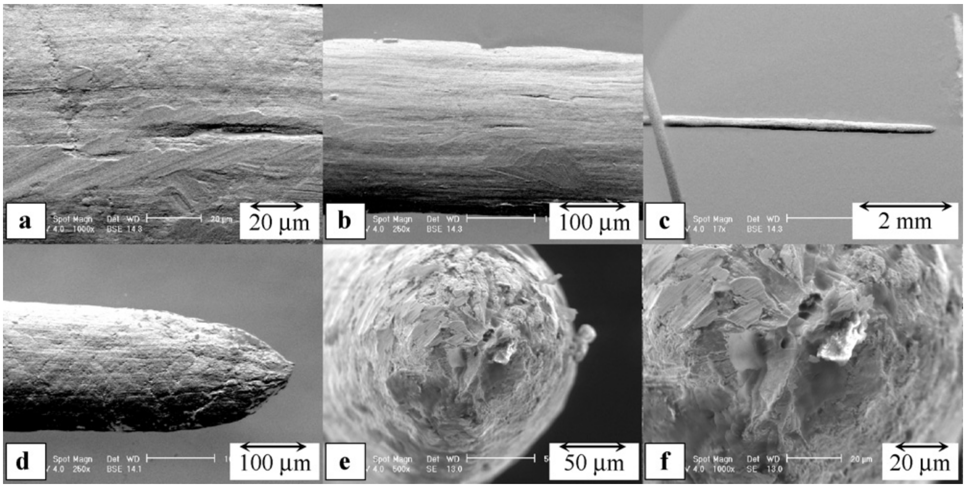

Fig. 7. SEM micrograph showing topographic contrast of wire which reached ~17% strain after experiment involving heating. (a-c) Side view far from the fracture site; (d) side view of the fracture site; (e and f) top view of the fracture surface.

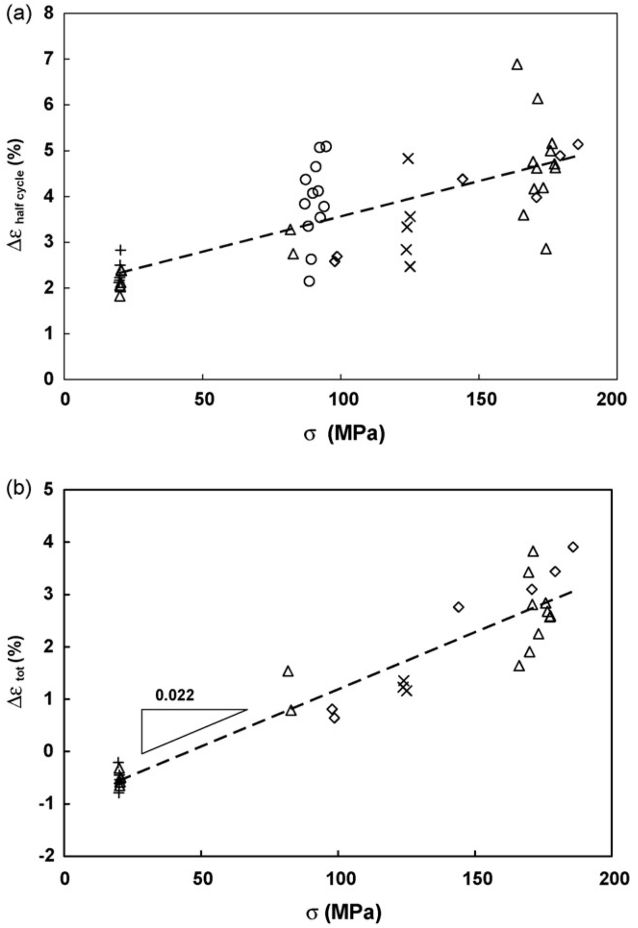

Fig. 8. Plot of strain increment accumulated over (a) a hydriding half cycle and (b) a full hydriding–dehydriding cycle vs. applied true stress. Each data point represents one half (or full) cycle and each symbol represents a distinct wire. The line is a linear least square best fit to all data points.

In these plots, cycles without full desorption and cycles involving heating under full load are not shown, whereas cycles involving heating with low load are included, since it was shown that moderated heating does not cause annealing [21,29]: Goltsov [29] demonstrated that while hydrogen decreases the recrystallization temperature of Pd, it remains above 200–250 °C.

As discussed in the Introduction, deformation under chemical cycling can be the result of internal stresses produced by two different mechanisms: lattice swelling gradient due to solute gradient, and volume mismatch due to the phase transformation. The diffusivity of hydrogen in Pd is given by [31]: $D = D_o \exp(-Q/RT)$, where $D_o = 2.9 \times 10^{-7}\,\mathrm{m^2/s}$, $Q = 22$ kJ/mol, T is the absolute temperature and R is the gas constant. At 300 K, the diffusivity of hydrogen in Pd is high at $4.3 \times 10^{-11}\,\mathrm{m^2/s}$. The typical diffusion time for a diffusion distance given by the wire radius ($r = 0.125$ mm) is $r^2/4D = 91$ s. Given that the total hydrogen absorption time takes many hours, and the desorption time is even longer, it can safely be assumed that the hydrogen gradient within the wire is negligible and the hydrogen profile is nearly flat within each phase. Moreover, the lattice volumetric swelling caused by hydrogen dissolving in Pd is only ~0.5% [17], as compared to ~10% [17] volumetric swelling caused by the Pd to Pd-hydride phase transformation. Considering the fast hydrogen diffusion, it is also reasonable to assume that the transformation does not occur radially following a front, but rather occurs randomly throughout the volume. This allows the use of a simple equation by Greenwood and Johnson [3], which predicts that the strain per cycle (metal → hydride → metal in the present case) $\Delta\varepsilon_{\mathrm{tot}}$ is:

$$\Delta\varepsilon_{\mathrm{tot}} \sim \frac{5}{3}\frac{\Delta V}{V}\frac{\sigma}{\sigma_{\mathrm{Y}}} \qquad (1)$$

where $\Delta V/V$ is the volume mismatch between the two different phases, σ_{Y} is the yield stress of the material deforming plastically to accommodate the internal mismatch and, as before, σ is the externally applied uniaxial stress. Experimental values for the total strain accumulated after a full hydriding–dehydriding cycle are plotted in Fig. 8b against the applied stress σ. A reasonable linear fit can be used to describe the data, as predicted by Eq. (1), with a slope $\Delta\varepsilon_{\mathrm{tot}}/\sigma = 0.22\,\mathrm{GPa^{-1}}$. Using the volumetric mismatch $\Delta V/V = 0.1$ [17], Eq. (1) can be solved for the yield stress of Pd, providing a value $\sigma_{\mathrm{Y}} = 760$ MPa. This value is much higher than that measured on the as-received wires (350 MPa) and that reported for cold-worked Pd wires (290 MPa [22]), indicating that the hydride–dehydride cycles work-harden the metal due to the large volume mismatch inducing internal plasticity. The calculated yield stress value is also 50–70% higher than those obtained by Goltsov (450–500 MPa) [24] after hydriding–dehydriding cycles at 100 °C. This can be explained qualitatively by the lower temperature used in our experiments, resulting in a higher volume change during hydrogenation (because of the wider miscibility gap between the metal and hydride) and a lower dislocation mobility, both of which lead to increased work-hardening during transformation. Also, the maximum applied stress used here was 190 MPa, which is one quarter of the value of the yield stress calculated above. This justifies the use of Eq. (1), which is valid only for stress small as compared to the yield stress. For higher values, a non-linear model [32] becomes necessary.

It is apparent in Fig. 8b that the best-fit line does not cross the origin, as predicted by Eq. (1). This is most likely due to ratcheting, which has also been observed in titanium samples subjected to hydrogen cycles [2], and is discussed earlier with respect to Fig. 3.

4. Conclusions

Swaged Pd wires were subjected to hydrogen charging–discharging cycles under a constant uniaxial stress. Strain increments are observed after each cycle, and they can be accumulated upon multiple cycles up to a total strain as high as ~40%. As the number of hydrogen charging–discharging cycles increases, the desorption kinetics become more sluggish. Accelerating the desorption kinetics by Joule heating of the wire results in fracture after ~17% tensile strain due to partial necking causing local heating.

Strain per cycle is proportional to applied stress, in agreement with prediction by the Greenwood–Johnson model for transformation mismatch plasticity, and as previously observed in titanium subjected to hydrogen cycles. The model predicts a yield stress of ~760 MPa for hydrogen-cycled Pd, which is much higher than the initial yield stress of the wires, and ~50% higher than previous values reported for Pd hydrogen cycled at elevated temperature with no applied stress.

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