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# High-pressure torsion of palladium: Hydrogen-induced softening and plasticity in ultrafine grains and hydrogen-induced hardening and embrittlement in coarse grains

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ABSTRACT

Pure Pd (99.9%) was processed by high-pressure torsion (HPT) to form an ultrafine-grained (UFG) structure with an average grain size of ~220 nm, high hardness of 175 Hv, high tensile strength of 650 MPa and appreciable plasticity of 20%. Tensile tests showed that, unlike coarse-grained sample in which a hydrogen-induced embrittlement and hardening occurred, a hydrogen-induced softening and plasticity occurred in the HPT-processed UFG sample. A hydride phase formed after exposing the samples to hydrogen, while the formation of hydride was facilitated by the HPT processing. The hydride phase was decomposed by holding the samples in the air for prolonged time, but the hydride phase was more stable after HPT processing.



## 1. Introduction

To achieve ultrafine-grained (UFG) metals with high strength and appreciable ductility, a great attention has been allocated to the application of high-pressure torsion (HPT) [1–6]. The HPT process, which was first introduced by Bridgman in 1935 [1], is a useful severe plastic deformation (SPD) procedure for significant refinement of microstructures in metallic materials. In the HPT method, a disc sample is placed between two anvils under a high pressure and intense shear strain, $\gamma$ ($\gamma = 2\pi rN/h$, $r$: distance from disc center, $N$: number of turns, $h$: disc thickness), is introduced by rotating the two anvils with respect to each other [1–6]. Despite numerous reports on the mechanical property evolution in the HPT-processed UFG metals (see reviews in Refs. [1–6]), there are limited reports on the mechanical properties of SPD-processed materials in the presence of hydrogen [7–14].

It is well known that many metals such as Mg, Ti, Zr, Hf, Nb, V and Pd produce hydrides in the atmosphere of hydrogen under high pressures. Metal hydrides are considered as potential candidates for solid-state hydrogen storage [15,16]. The influence of SPD on hydrogen storage performance of metal hydrides was investigated in several papers and improvement on hydrogenation kinetic [17–32], hydrogen diffusion [33] and hydrogenation activation [34,35] has been reported. Moreover, it was shown that HPT is effective for the formation of strain-induced hydride [36] as well as for the formation of vacancy-hydrogen complexes [37,38]. Despite these reports, little is understood to date regarding the thermodynamics of hydrogen storage after grain refinement by SPD.

This study is thus initiated to examine the hydrogen absorption and desorption behavior associated with hydride formation and decomposition in an ultrafine-grained structure of HPT-processed pure Pd. While the experiment is undertaken in comparison with a coarse-grained structure after fully annealing, the study further examines the effect of the hydrogenation on the mechanical properties.

## 2. Experimental materials and methods

A rod of pure Pd (99.9%) with 10 mm diameter and 50 mm length was used in this study. The rod was sliced to discs with

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thicknesses of 0.9 mm using a wire-cutting electric discharge machine. The discs were encapsulated in an argon-filled silica tube and were further annealed for 3 h at 1073 K within the tube to eliminate deformation history and to give an average grain size of ~75 μm.

HPT was conducted at room temperature on the annealed discs. A set of upper and lower anvils with a circular flat-bottom hole at the center, made from tool steel having a nitrified surface with the roughness of ~30 μm, were used to process the disc samples. The hole depth was 0.25 mm and the hole diameter was 10 mm. The disc samples were processed for $N=0.5$, 2 and 10 turns under a pressure of $P=6$ GPa with a rotation speed of $\omega=0.25$ rpm. Samples after annealing and after processing with HPT for 10 turns were further exposed to hydrogen atmosphere at 298 K under a pressure of 0.1 MPa or 8 MPa for 1 h.

The discs after annealing, after HPT processing and after exposure to hydrogen were evaluated using Vickers microhardness measurement, optical microscopy (OM), electron back-scatter diffraction (EBSD) analysis, X-ray diffraction (XRD), tensile test and hydrogen storage analysis.

First of all, after processing by HPT, the discs were polished to a mirror-like surface and the Vickers microhardness was measured with an applied load of 300 g for 15 s along the radii from the center to edge at 8 different radial directions with 1 mm increments.

Second, for OM observations, discs were first mechanically polished to mirror-like surfaces and further subjected to electrochemical polishing in a solution of 5.3 g LiCl, 11.2 g $Mg(ClO_4)_2$, 100 $cm^3$ $CH_3(CH_2)_3O(CH_2)_2OH$ and 500 $cm^3$ $CH_3OH$ (BK-2 electrolyte) at 298 K under an applied voltage of 10 V.

Third, for EBSD, the discs prepared by electro-polishing for OM observations were examined using a scanning electron microscope at a voltage of 20 kV and the crystal orientations were determined using an automated beam scanning system with a step size of 7.5 nm and a probe size of 10 nm.

Fourth, crystallographic structures were evaluated in a ~3 mm diameter region at the edge of the discs by XRD analysis using the Cu Kα radiation.

Fifth, miniature tensile specimens having dimensions of 1.5 mm gauge length, 0.6–0.7 mm width and 0.5 mm thickness were cut from the discs at the position 2 mm away from the center. Each tensile specimen was mounted horizontally on grips and pulled to failure using a tensile testing machine with an initial strain rate of $2\times10^{-3}$ $s^{-1}$.

Sixth, the hydrogen pressure–composition ($P$–$C$) isotherms were measured using one disc sample with a total weight of ~0.5 g in a Sieverts-type gas absorption apparatus at 348 K, 373 K and 398 K in the pressure range of 0.2–400 kPa.

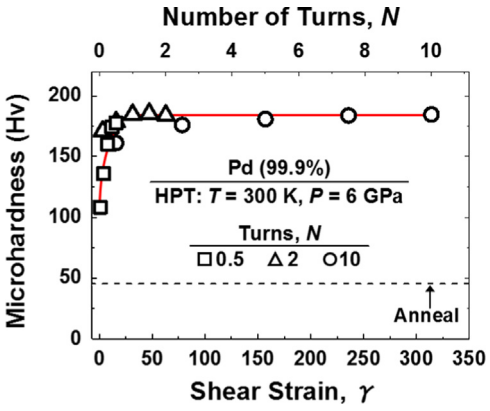


**Fig. 1.** Vickers microhardness plotted against shear strain for samples processed by HPT for various turns, including hardness level after annealing for 1073 K for 3 h.

## 3. Results and discussion

### 3.1. Evolution of hardness and microstructure after HPT

Fig. 1 plots the microhardness against shear strain for pure Pd after $N=0.5$, 2 and 10 turns. The hardness increases with increasing shear strain at an early stage of straining but saturates to a steady state at high strains where the hardness remains unchanged with further straining. The hardness at the steady state is 175 Hv, which is 3.7 times higher than the hardness of the annealed sample. The shape of the hardness versus strain curve for pure Pd is similar to those for metals with high melting temperatures [39–42], numerous alloying systems [43–45] and many intermetallics [34,46]. It is considered that the steady state appears because of a balance between the hardening and the softening, where the hardening is due to dislocation accumulation and grain refinement whereas the softening is due to annihilation of dislocations through recovery, recrystallization and grain boundary migration [6].

An OM micrograph after annealing but before HPT is shown in Fig. 2(a) and an orientation map analysis using EBSD for the sample processed after 10 turns is shown in Fig. 2(b). Observation

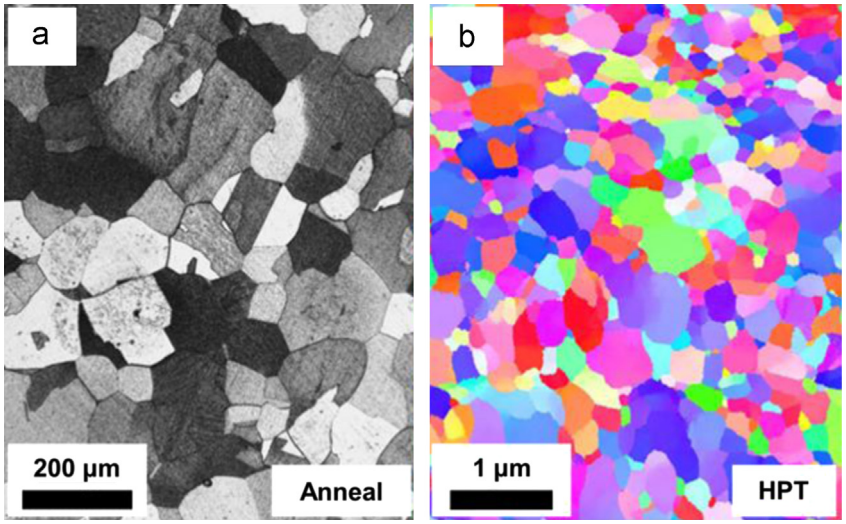


**Fig. 2.** (a) OM micrograph after annealing at 1073 K for 1 h and (b) EBSD orientation map after HPT for 10 turn. Step size for EBSD orientation mapping was 7.5 nm.