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Hydrogen behavior in ultrafine-grained palladium processed by high-pressure torsion

Hideaki Iwaoka [a,b,*], *Zenji Horita* [a,b]

[a] *Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan*

[b] *WPI, International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan*

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ABSTRACT

Hydrogen permeation tests were carried out on ultrafine-grained palladium processed by high-pressure torsion (HPT) and the results were compared with those on an annealed coarse-grained state. It is shown that hydrogen diffusion is similar above 200 °C but is enhanced at temperatures below 200 °C in the ultrafine-grained state. All samples were subjected to X-ray diffraction analyses after the hydrogen permeation tests. It is shown that hydride formation occurs at lower temperatures in both coarse- and ultrafine-grained states but the hydride formation temperature is reduced to a lower temperature in the ultrafine-grained state. This study suggests that grain boundaries of palladium act as diffusion pass but not as the sites for hydride formation.

1. Introduction

It is important to investigate the hydrogen behavior in metals and alloys for hydrogen production, storage and utilization. Hydrogen may be trapped by lattice defects such as dislocations and vacancies and grain boundaries. However, there is controversy as to hydrogen interactions with grain boundaries as raised by Oudriss et al. [1,2]. Some studies reported that hydrogen diffusivity is enhanced by short-circuit diffusion along grain boundaries [3–7], whereas an opposite trend was reported in other studies that the grain boundaries act as trapping sites for hydrogen, thus decreasing the hydrogen diffusivity [8–10].

Solving this controversy has been restricted because of the difficulty of preparing nanograin-structured metals and alloys having abundant grain boundaries in a bulk form of samples. Conventional rolling and drawing processes may refine the grain size to the order of a few micrometers but the grain size is still insufficient to investigate the effect of grain boundary because the volume fraction of the grain boundary is very few in this range of the grain size [11].

Since it was reported that grain refinement to the nanoscale leads to marked improvement of mechanical properties including various physical properties, production of nanograined materials has gained great interest. Several methods are available for the production of nanograins, such as gas

* *Corresponding author*. Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan. Tel./fax: +81 92 802 2992.
E-mail address: iwaoka@zaiko6.zaiko.kyushu-u.ac.jp (H. Iwaoka).

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deposition [12], electrical deposition [13] and severe plastic deformation (SPD) process [14]. Although gas deposition and electrical deposition have been used for the grain refinement and the investigation of grain boundary effect on hydrogen behavior [1–5,15–17], SPD process has hardly been used.

The SPD process includes Equal-Channel Angular Pressing (ECAP) [18], Accumulative Roll-Bonding (ARB) [19] and High-Pressure Torsion (HPT) [20]. Theoretically, these processes can introduce strain infinitely because sample shape does not change with processing and the processing can be repeated. Therefore, ultrafine grains with sizes of hundreds nanometer can be obtained even pure metal. Especially, the HPT process can produce smaller grains than the other SPD processes [21].

In HPT processing, a disk sample is placed between upper and lower anvils and the lower anvil is rotated with respect to the upper anvil under a high pressure. Large strain is then introduced and grain refinement to the submicrometer and/or nanometer range is achieved by the HPT processing. Application of high pressure during the HPT operation prevents cracks and voids from formation. In addition, no impurity is introduced into the sample during the HPT processing unlike the grain refinement using the processes of gas deposition and electrical deposition. Therefore, it is anticipated that evaluation becomes more reliable for the interaction of hydrogen with grain boundaries. In this study, HPT process is applied to palladium which has active interaction with hydrogen. Thus, hydrogen behavior in ultrafine-grained palladium is examined using gas permeation test in comparison with annealed palladium which has less dislocations and grain boundaries.

2. Experimental procedures

High purity palladium (99.9%) in the forms of sheet with 0.5 mm thickness and of rod with 10 mm diameter was used in the present investigation. The Pd sheet was cut to disks with 8.9 mm diameter and 0.5 mm thickness and annealed at 1073 K for 10.8 ks, giving a grain size of ~80 μm (hereafter referred to Annealed sample). The Pd rod was cut to disks with 2.6 mm thickness and pressed with HPT anvils under a pressure of 1.5 GPa–20 mm diameter disks having the same size as the anvil hole. The pressed disks were annealed at 1073 K for 10.8 ks and then processed by HPT at room temperature under a pressure of 1.5 GPa with a rotation speed of 0.25 rpm for 10 turns (hereafter referred to HPT-processed sample).

Disks with 8.9 mm diameter were extracted from the HPT-processed disks at 5 mm off-axis positions as shown in Fig.1 for permeation test. The annealed and HPT-processed disks were ground to 0.425 ± 0.005 mm thicknesses and polished to a mirror-like surface. Each disk was cleaned by an ultrasonic bath with acetone before permeation test.

An annealed or HPT-processed disk was placed at the joint of two pipes so that the disk separates two chambers: one with hydrogen gas flow and the other with argon gas flow as illustrated in Fig. 2. The flow rates of these gases were controlled as 30 cc/min for hydrogen gas and 10 cc/min for argon gas. Placing the system (as Fig. 2) in a furnace, permeation tests were conducted at a selected temperature in a range from 100 to 500 °C. Mixed gas of argon and hydrogen as a consequence of permeation through the disk was taken by

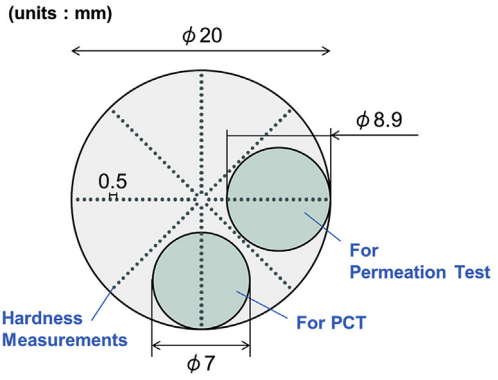

Fig. 1 – Disk sample and positions of permeation test, PCT measurement and hardness measurement.

microsyringe and the hydrogen concentration in the mixed gas was measured by gas chromatography. Hydrogen flux (J_{H_2}) was calculated by the following equation,

$$J_{H_2} = \frac{C_{H_2}}{1 - C_{H_2}} \frac{Q_{Ar}}{A} \quad (1)$$

where C_{H_2} is the hydrogen concentration, Q_{Ar} is the flow rate of argon gas, A is the cross-sectional area of the disk.

X-ray diffraction (XRD) analysis was conducted using the Cu Kα radiation on the annealed and HPT-processed disks after permeation test. It should be noted that the disk was kept in the unit of permeation test after stopping hydrogen flow at the testing temperatures for 3 h to remove the hydrogen in the lattice because hydrides may form when the disk is removed with hydrogen left in the lattice. For comparison, the annealed disk and HPT-processed disk before the permeation tests were also analyzed. LaB_6 powders were used as a standard sample for correcting any possible peak shift between measurements.

The Vickers microhardnesses were measured on the annealed and HPT-processed disks before the permeation testing. The measurements were made, as illustrated in Fig. 1, along 8 radial directions at distances from the disk center with spacing of 0.5 mm under a load of 100 g for 15 s. The average hardness was determined from the 8 measurements at the equal distance from the disk center.

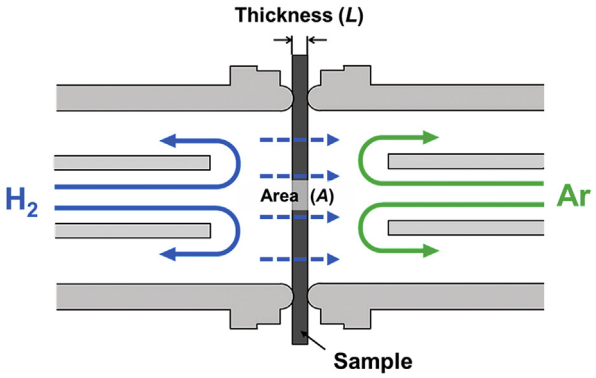

Fig. 2 – Schematic illustration for gas permeation test.