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Hydrogen diffusion in ultrafine-grained palladium: Roles of dislocations and grain boundaries

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ABSTRACT

Diffusion behavior of hydrogen in ultrafine-grained palladium (Pd) is investigated by electrochemical permeation tests. The ultrafine-grained structure is produced by severe plastic deformation through high-pressure torsion (HPT). The diffusion behavior is compared with an annealed state with a coarse-grained structure and a cold-rolled state with dislocations and subgrain structures. Hydrogen permeation is analyzed in absorption step and desorption step at five different temperatures in the range of 15 −35 °C. Hydrogen diffusion is retarded due to hydrogen trapping by dislocations. Grain boundaries act as rapid diffusion paths for hydrogen so that hydrogen diffusion is enhanced in the HPT-processed Pd samples with the ultrafine-grained structures.

1. Introduction

Lattice defects in metallic materials have important interaction with hydrogen atom related to deformation behavior including fracture. Because dislocations often act as trapping sites, hydrogen diffusion in a rolled metal may be delayed by a high-density of dislocations [1–6]. By contrast, hydrogen may enhance dislocation mobility, and thus makes it easy for plastic deformation to occur at hydrogen-rich areas [7]. This effect is called “hydrogen enhanced localized plasticity (HELP)” and is thought to be one of the mechanisms for hydrogen embrittlement. Meanwhile, hydrogen on grain boundaries weakens the metallic bond and causes intergranular fracture. Accordingly, it is important to clarify whether hydrogen is trapped by grain boundaries or passes rapidly through the grain boundaries. However, many researchers have provided different views on hydrogen behavior in grain boundaries. Until now, a controversy exists as to the role of the grain boundaries on the hydrogen diffusion. There are some reports that hydrogen diffusion coefficient increases because the grain boundaries act as fast diffusion paths [8–21], whereas other reports that hydrogen diffusion coefficient little varies because grain boundary has little effect on hydrogen diffusion or decreases because the grain boundaries act as trapping sites [22–29].

Pederson et al. [30] simulated hydrogen diffusion along grain boundaries in Al by a Monte Carlo method and showed that there is a difference in hydrogen behavior between tilt boundaries and twist boundaries. Using electron back-scattering diffraction (EBSD) analysis, Oudriss et al. [31] measured the distribution of grain boundary characters. With reference to the results of hydrogen permeation tests, it was suggested that low-energy grain boundaries consisting of low-angle boundaries and special boundaries act as hydrogen trapping sites, and high-energy boundaries having random boundaries acts as fast diffusion path. Lee et al. [10,32,33] and Mine et al. [21,34] compared the hydrogen behavior in the grain boundaries of a body-centered cubic (BCC) metal and a face-centered cubic (FCC) metal. They concluded that the grain boundaries act as trapping sites in the BCC metal and fast diffusion path in the FCC metal. Kirchheim et al. [35,36] revealed that hydrogen diffusion in nanostructured palladium increases with hydrogen concentration; that is hydrogen diffusion in nanostructured palladium is lower than that in single crystal at low hydrogen concentration and is higher at high hydrogen concentration. There is no simple relation between the grain boundaries and hydrogen behavior because several factors described above affect the determination of the role of the grain boundaries. Therefore, extensive study is needed for accurate understanding of hydrogen diffusion in the grain boundaries.

It is preferable that fine-grained samples are used for investigation of grain boundaries effect. In the present study, high-

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pressure torsion (HPT) processing [37] was used for production of a submicrometer-grained structure. A disk sample is placed between shallow holes of the anvils. Then, torsional strain is introduced to the sample by rotation of the lower anvil under a high pressure as shown in Fig. 1. HPT processing can be applicable to high strength materials or brittle materials because applied high pressure reduce the development of crack and void during deformation. It is an advantage of using the HPT process that a wider range of metals can be selected as samples for investigation.

However, there are few attempts to reveal the grain boundary effect on hydrogen behavior using ultrafine-grained metals processed by HPT. In this study, HPT-processed samples are used for electrochemical permeation and compared the results of an annealed sample containing little lattice defect and a cold-rolled sample containing a high dislocation density. Palladium was selected as the test sample because its surface has high resistance to oxidation and carbon contamination [38], and hydrogen atoms can permeate with little effect by surface reaction from hydrogen molecules.

2. Experimental procedures

2.1. Experimental materials and their microstructure

High purity Pd (99.9% purity) disks having 8.9 mm diameter and 0.35–0.40 mm thickness were prepared for electrochemical permeation tests with the following three different states: annealed disk, rolled disk and HPT-processed disk.

A Pd sheet with 0.5 mm thickness was cut to disks with 8.9 mm diameter and annealed at 1273 K for 10.8 ks(hereafter referred to annealed disk). A Pd rod with 10 mm diameter and 50 mm length was cut to disks with 1.0 mm thickness and 2.6 mm thickness. The disks with 1.0 mm thickness were annealed and then cold-rolled with a rolling reduction of 50% (hereafter referred to rolled disk). The disks with 2.6 mm thickness were pressed with HPT anvils having shallow holes at the centers with 20 mm diameter and 0.25 mm depth under a pressure of 1.5 GPa. The pressed disks were annealed 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 disk).

The HPT-processed disk has an inhomogeneous structure because the strain introduced by HPT-processing increases with the distance from the disk center [39,40]. However, the variation of microstructure is saturated with straining so that the disk for permeation test was selected from periphery areas where the saturation was well reached in the HPT-processed disk to extract homogeneous 8.9 mm disks as described in an earlier report [41].

Microstructural information including grain boundary character and dislocation density of Pd after cold rolling and HPT-processing was obtained by electron back-scatter diffraction (EBSD) and X-ray diffraction (XRD) analyses.

TSL orientation imaging microscopy (OIM) was performed using a Hitachi SU6600 scanning electron microscope (SEM) for determination of grain size as well as grain boundary character from EBSD patterns. Samples were ground mechanically with alumina suspension to mirror-like surfaces and electropolished with a BK-2 electrolyte (5.30 g LiCl [lithium chloride], 11.16 g $Mg(ClO_4)_2$ [magnesium perchlorate], 100 ml $CH_3(CH_2)_3O(CH_2)_2OH$ [butyl cellosolve] and 500 ml CH_3OH [methanol]) [42]. SEM was operated with different accelerating voltages: 15 kV for rolled disks having larger grain sizes as ~100 μm and 20 kV for HPT-processed disks having smaller grain sizes as ~350 nm.

A modified Warren-Averbach method [43] was used for estimation of dislocation density from X-ray diffraction profiles obtained by a Rigaku RINT-2100 X-ray diffractometer (XRD). The Cu Kα line was used for the measurement of diffraction profiles with a tube voltage of 40 kV and a tube current of 40 mA.

2.2. Electrochemical permeation test

Fig. 2 shows a schematic illustration of an electrolytic cell used for the present electrochemical permeation test. The cell consists of two L-shaped acrylic tubes: one is the anode cell and the other is

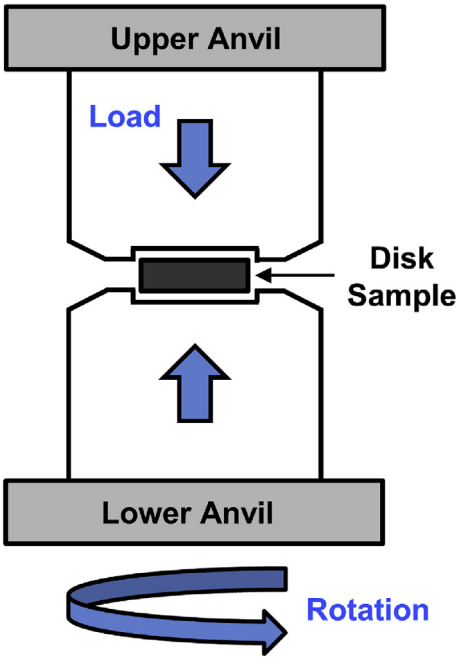

Fig. 1. Schematic illustration of HPT facility.

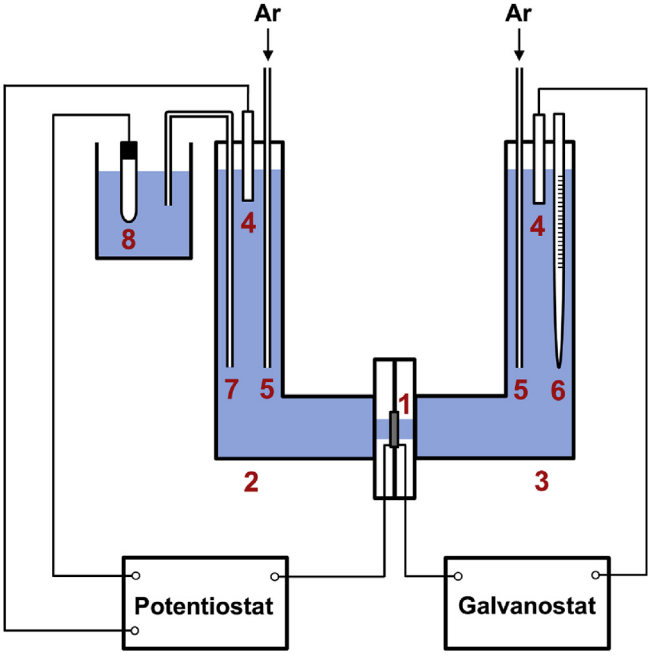

Fig. 2. Schematic illustration of electrolytic cell used for present electrochemical permeation test: 1) disk specimen, 2) anode cell, 3) cathode cell, 4) counter electrode (Pt), 5) gas flow tube, 6) thermometer, 7) salt bridge, 8) reference electrode.