Acta Materialia 107 (2016) 168-177

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat



Full length article



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



Hideaki Iwaoka ^{a, b, *}, Makoto Arita ^a, 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

ARTICLE INFO

Article history: Received 24 August 2015 Received in revised form 18 December 2015 Accepted 26 January 2016 Available online 9 February 2016

Keywords: High-pressure torsion Grain boundary diffusion Palladium Hydrogen

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.

© 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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].

* Corresponding author. E-mail address: iwaoka@zaiko6.zaiko.kyushu-u.ac.jp (H. Iwaoka).

http://dx.doi.org/10.1016/j.actamat.2016.01.069

1359-6454/© 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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 facecentered 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, highpressure 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



Fig. 1. Schematic illustration of HPT facility.

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(ClO₄)₂ [magnesium perchlorate], 100 ml CH₃(CH₂)₃O(CH₂)₂OH [butyl cellosolve] and 500 ml CH₃OH [methanol]) [42]. SEM was operated with different accelerating voltages: 15 kV for rolled disks having larger grain sizes as ~100 μ m 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 K α 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. 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.



Fig. 3. Orientation map (a) and grain boundary maps color-coded according to misorientation (b) and grain boundary character (c) for rolled disk and HPT-processed disk of Pd. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the cathode cell. An electrolytic solution of 0.2 N NaOH was filled in both cells, and a disk sample was placed between the two cells to prevent the electrolytic solutions from mixing with each other.

Hydrogen is generated on the sample surface by applying a current in the cathode cell:

$$2H^+ + 2e^- \rightarrow H_2$$
.

This hydrogen permeates to the anode side and is oxidized to hydrogen ion:

$$H_{met} \rightarrow H^+ + e^-$$

Hydrogen permeation rate can be measured by tracking the current generated from the above reaction. Hereafter, the cathode side and the anode side are called as the charging side and the detection side, respectively, and the measured currents at the charging side and the detection side are called as the charging current and the permeation current, respectively. A saturated KCl–Ag/AgCl electrode was used as a reference electrode.

Before permeation testing, the electrolytic solution was deaerated by argon gas and an open circuit potential of the detection side was measured. During the permeation testing, the electrode potential in the anode cell was controlled by a potentiostat at the same value as the open circuit potential value, which is sufficient to oxidize hydrogen.

The permeation test includes two steps: absorption step and desorption step. In the absorption step, temporal variation in the permeation current is measured while applying the charging current until the permeation current saturates. After the saturation, the desorption step starts upon stopping the current for hydrogen



Fig. 4. Misorientation angle distribution for rolled and HPT-processed disks of Pd.

charging. Then, hydrogen going out of the sample to the anode side is measured.

Diffusion coefficient (D) can be calculated using the following relation [44] with the break-through time (t_b) which is defined as the intersection of the time axis with the tangential line at an inflection point in the permeation curve,

$$D = 0.76 \frac{L^2}{\pi^2 t_b}$$
(1)

where *L* is the disk thickness. The diffusion coefficients in the absorption step (D_{abs}) and the desorption step (D_{des}) are then obtained from the measured values of t_b .

3. Results and discussion

3.1. Difference of microstructure

Fig. 3(a) shows color-coded orientation maps obtained by EBSD analysis. The rolled disk and the HPT-processed disk were observed from the direction normal to the rolling plane and the pressing direction, respectively. The rolled disk consists of grains which are elongated in the rolling direction with ill-defined grain boundaries having low-angles of misorientation, whereas the HPT-processed disk has equiaxed grains with an average size of ~350 nm with well-defined grain boundaries having high-angles of misorientations.

Grain boundaries in Fig. 3(b) are distinguished according to the degrees of misorientations for comparison of the misorientation distribution between the rolled disk and the HPT-processed disk. The black and blue lines correspond to low-angle boundaries with misorientations of $2^{\circ} \sim 5^{\circ}$ and $5^{\circ} \sim 15^{\circ}$, respectively. The red line corresponds to high-angle boundaries with misorientations more than 15° . Fig. 4 is distributions of misorientation angle for the rolled and HPT-processed disks. The fraction of high-angle

Table 1
Grain boundary character distribution for rolled and HPT-processed disk of Pd.

	Low-angles	Coincidence Σ3-29	Random Σ>29
Rolled HPT	77.7 23.2	3.4 9.4	18.9 67.4
			(Unit:%)

(a) Absorption



(b) Desorption



Fig. 5. Permeation curves at a charging current density of 5 A/m^2 and test temperature of 20 °C in (a)absorption step and (b)desorption step.

boundaries in the HPT-processed disks is higher than that in the rolled disks. In Fig. 3(c), high angle boundaries are delineated with three different colors: blue, green and red for coincidence boundaries with $\Sigma = 3$ and $\Sigma 5-29$ and random boundaries, respectively. Table 1 compares the fractions of the grain boundary characters including low-angle boundaries between the rolled and HPT-processed disks. Random boundaries result in a large fraction in the HPT-processed disks.

In this study, dislocation densities of the rolled disk and the HPT-processed disks were further determined using a modified Warren-Averbach analysis. Thus, it follows from the XRD profiles that the dislocation densities are 6.5×10^{14} m⁻² and 8.4×10^{14} m⁻² for the rolled disk and the HPT-processed disk, respectively. Kirchheim et al. reported the value of 6.0×10^{14} m⁻² for the dislocation density of palladium after 50% cold rolling [45] and this is consistent with the value measured in the present study.

In summary, therefore, the HPT-processed disk has higher densities of dislocations and high-angle boundaries with random

(a) Absorption



(b) Desorption



Fig. 6. Magnified figures in early stage of Fig. 5.

characters than the cold-rolled disk.

3.2. Hydrogen permeation tests

Fig. 5 is the results of permeation tests at a charging current density of 5 A/m^2 and a test temperature of 20 °C for (a) the absorption step and (b) the desorption step. Permeation current which is normalized by the maximum value is plotted against the time which is normalized by the square of the sample thickness. The permeation current for the HPT-processed disk saturates earlier than those for the other disks in both absorption and desorption steps. Fig. 6 is an enlargement of the early stage in Fig. 5 to closely examine the permeation behavior including the break-through time, t_b . For the absorption step in (a), t_b is the shortest in the annealed disk and the longest in the rolled disk. For the same as in the annealed disk and in the HPT-processed disks to less than that in the annealed disk.

The permeation behavior in the absorption step and the desorption step is usually different when trapping sites are present





Fig. 7. Schematic illustration of hydrogen permeation behavior in metal including lattice defect in (a)absorption step and (b)desorption step. Charging and detection side are indicated by "C" and "D" in the figure, respectively.

in the sample [46]. Fig. 7 illustrates the difference of the hydrogen permeation behavior between (a) the absorption step and (b) the desorption step. In an early stage of absorption (Fig. 7 (a)), hydrogen atoms cannot reach the detection side because they are trapped by the trapping sites and this continues until a certain quantity of trapping sites are occupied by trapped hydrogen atoms. However, in the desorption step (Fig. 7 (b)), the trapping sites have already been occupied by trapped hydrogen atoms so that hydrogen atoms can move to the detection side without interruption by the trapping effect.

It is obvious from the above interpretation that t_b in the absorption step was affected by hydrogen trapping in both the rolled disk and the HPT-processed disk. In the desorption step, t_b of the rolled disk is almost the same as the annealed disk because trapping sites are occupied by hydrogen atoms. This indicates that dislocations act as trapping sites for hydrogen as reported in other published papers [1–6]. It should be noted that t_b of the HPTprocessed disk also decreases in the desorption step when compared with the value in the absorption step, but nevertheless it becomes shorter than those of the rolled and annealed disks. In



Fig. 8. Diffusion coefficient calculated from break-through time of permeation curve against charging current density.

addition, the permeation current changes more quickly for the HPT-processed disk in both the absorption and desorption processes. All these results indicate that hydrogen diffusion is accelerated only in the HPT-processed disk because of a high density of high-angle grain boundaries with random character.

3.3. Diffusion coefficient

Figs. 8 and 9 plot the diffusion coefficient, *D*, against the charging current density and reciprocal temperature, respectively. Here, the values of *D* were calculated through eq. (1) using t_b and *L* in the permeation tests. The horizontal dotted lines in all graphs represent the diffusion coefficient of the annealed disk in the absorption step at 25 °C and they are drawn to make comparison of each graph easier.

Several important points arise from the measurements of *D* in Fig. 8. First, the values of *D* in the annealed disk are independent of

the charging current density and this is regardless of whether it is in the absorption or desorption step (Fig. 8(a)). Second, the values of *D* in the rolled disk and the HPT-processed disk increase with the charging current density and this dependence is more prominent in the absorption step than in the desorption step (Fig. 8(b) and (c)). Third, the values of *D* in the absorption step are always lower that in the desorption step for both rolled and HPT-processed disks (Fig. 8(b) and (c)). Fourth, the values of *D* in the absorption step are invariably lower in the rolled disk and the HPT-processed disk than in the annealed disk (Fig. 8(a), (b) and (c)). Fifth, the values of *D* in the desorption step for the rolled disk and the HPT-processed disk are slightly smaller than and well above for the annealed disk, respectively (Fig. 8(a), (b) and (c)). Similar trends are also derived from Fig. 9.

In Fig. 9, it is apparent that the measured D values are well represented by a linear form of the reciprocal temperature, indicating that the following Arrhenius relation reasonably holds for



Fig. 9. Diffusion coefficient calculated from break-through time of permeation curve against reciprocal temperature: Arrhenius plots.

the whole measurements.

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

where D_0 is the frequency factor, Q is the activation energy for hydrogen diffusion, R is the gas constant and T is the absolute temperature. Inspection of Fig. 9 reveals that the temperature dependence of D (i.e., Q) including the magnitude of D (i.e., D_0) is almost the same in the absorption and desorption steps for the annealed disk. However, they deviate from the annealed state for both the rolled and HPT-processed states. The values of D_0 and Q are then evaluated quantitatively. First, average values of D_0 and Qobtained from Fig. 9 (a) in the annealed disk are $D_0 = 2.33 \times 10^{-7} \text{ m}^2/\text{s}$ and Q = 21.8 kJ/mol for the absorption step and $D_0 = 4.97 \times 10^{-7} \text{ m}^2/\text{s}$ and Q = 23.6 kJ/mol in the desorption step. These values are very similar to the average of literature values: $D_0 = 2.36 \times 10^{-7} \text{ m}^2/\text{s}$ and Q = 21.8 kJ/mol [47-57].

The values of O and D_0 in the rolled disk and the HPT-processed disk can also be determined at the given charging current densities. They are plotted against the charging current density in Fig. 10 (a) and (b), respectively. Both Q and D_0 in the annealed and cold-rolled disks are almost the same in the desorption step, whereas those in the absorption step are different between the annealed and coldrolled disks with higher values in the cold-rolled disks than in the annealed disks. This suggests that the mechanism for the hydrogen diffusion is the same once the trapping sites such as dislocations are occupied by trapped hydrogen as found from the desorption step. However, when trapping sites are available as in the absorption step, more energy is required for the hydrogen diffusion because they are trapped other than the normal flow without trapping as illustrated in Fig. 7. The hydrogen diffusion in the HPT-processed disks is different from that in the annealed and cold-rolled disks. This is because many grain boundaries in random

(a) Activation energy



Fig. 10. (a) Activation energy and (b) frequency factor for hydrogen diffusion plotted against charge current density.

nature are available and they act as rapid diffusion paths for hydrogen. Close inspection of Fig. 10 reveals that Q and D_0 increase with increasing the charge current density. Zener showed that there is a correlation between D_0 and Q for the diffusion in crystalline metals [58]. D_0 for interstitial diffusion in cubic lattice can be written as

$$D_0 = \frac{1}{6} l^2 n \nu \exp\left(\frac{\Delta S}{R}\right) \tag{3}$$

where *l* is the jump distance of a diffusion atom, *n* is the number of the paths which a diffusion atom can jump, *v* is the attempt frequency and ΔS is the activation entropy for diffusion. For FCC metals, *l* equals to the distance of adjacent octahedral sites ($=a/\sqrt{2}: a$ is the lattice constant), *n* equals to the number of adjacent octahedral sites (= 12) and ΔS follows the relationship as [58].

 $\Delta S = \lambda \beta Q / T_m \tag{4}$

here, λ is a numerical coefficient ($\lambda = 1$ for interstitial diffusion), β is dimensionless quantity related to elastic modulus and T_m is the

melting temperature. D_0 can then be expressed as a function of Q as

$$D_0 = a^2 \nu \exp\left(\frac{\beta Q}{RT_m}\right) \tag{5}$$

Thus, Fig. 11 plots the values of $\ln D_0$ against Q for the HPTprocessed disks in the desorption step. It is found that a good linear relation holds between $\ln D_0$ and Q. However, drawing Eq. (5) using the values as a = 0.389 nm, $\nu = 10^{13} \text{ s}^{-1}$, $\beta = 0.18$ [58] and $T_m = 1825$ K for Pd, the values of $\ln D_0$ are invariably lower with a higher slope for the HPT-processed disks than the one predicted by Eq. (5). Although Kirchheim and Huang commented that the relationship between $\ln D_0$ and Q involves less physical meaning [59], a tentative comparison is made in Fig. 11 by including results reported by Kirchheim et al. [60] and Lee et al. [61] for hydrogen diffusion in amorphous Pd alloys measured with changing the hydrogen concentration. They are much closer to the present results. This similarity seems reasonable because random boundaries in the HPT-processed disk can be regarded as regions having amorphous structure [62], and thus indicates that hydrogen atoms diffuse in random boundaries in the HPT-processed disks.

Finally, we discuss the diffusion behavior in grain boundary with



Fig. 11. Correlation between $\ln D_0$ and *Q* for hydrogen diffusion in HPT-processed Pd in the desorption step (circles) and in amorphous alloys (dotted line [60] and dashed line [61]). Solid line was drawn according to Eq. (5).

respect to charging current density (namely, hydrogen concentration). Kirchheim et al. reported that hydrogen diffusivity in grain boundary is enhanced with hydrogen concentration, as observed in Fig. 8 in the present study, due to a distribution of site energy associated with random structure [35]. Hydrogen atoms are preferentially trapped by the lower energy sites in the grain boundary at a low hydrogen concentration. As the hydrogen concentration increases, hydrogen atoms occupy the lower energy sites and begin to pass through the higher energy sites where the activation energy for diffusion is lower and hydrogen atoms can diffuse easily.

This interpretation agrees with the results that the activation energy for hydrogen diffusion in amorphous structure decreases with hydrogen concentration [60,61], but disagrees with the result of Fig. 10 in the present study. This discrepancy may be attributed to the difference in the fraction of disorder structure. Hydrogen atoms in the amorphous alloy mostly jump between disordered sites, whereas hydrogen atoms in the HPT-processed disk jump not only between disordered sites but also from lattice site to disordered site due to the lower fraction of disorder structure. Considering that there is a distribution in the activation energy for diffusion from lattice sites to grain boundary sites and when the hydrogen concentration is low, hydrogen atoms preferentially diffuse through the sites where the activation energy is low. However, as the hydrogen concentration becomes higher, those sites for higher activation energies contribute to the diffusion paths.

4. Summary and conclusions

- 1. The HPT-processed Pd disk consists of ultrafine grains with high-angle grain boundaries in random nature having the grain size of ~350 nm. The hydrogen behavior was then compared with those in the rolled disk where low-angle grain boundaries are more present but the dislocation density is almost the same.
- 2. In the absorption step, the hydrogen diffusion coefficients in the rolled disk and the HPT-processed disk are lower than that in the annealed disk because dislocations act as trapping sites. In the desorption step, there is little effect of the trapping site on the hydrogen diffusion in both rolled and HPT-processed disks because the trapping sites are already occupied during the absorption step. However, the hydrogen diffusion in the HPT-processed disk because random boundaries act as fast diffusion paths.

- 3. The activation energies for hydrogen diffusion in the annealed and rolled disks are invariable with the charge current density but that in the HPT-processed disks increases with the charging current density. This dependence is due to a disorder structure of random boundaries present more in the HPT-processed disks.
- 4. There is clear difference in the results of hydrogen permeation tests between the rolled disks and the HPT-processed disks. Thus, the bulk ultrafine-grained material obtained by HPTprocessing is useful for the investigation of hydrogen behavior in the grain boundary.
- 5. The hydrogen diffusion in the HPT-processed disks is similar to the one reported in amorphous alloys.

Acknowledgements

One of the authors (HI) would like to thank a Grant-in-aid for encouragement of young scientists in the faculty of engineering, Kyushu University. This work was supported in part by Grant-in-Aids from the MEXT, Japan (No. 22102004, No. 26220909 and No. 15K14183). The HPT process was carried out in the International Research Center on Giant Straining for Advanced Materials (IRC-GSAM) at Kyushu University.

References

- R.A. Oriani, The diffusion and trapping of hydrogen in steel, Acta Metall. 18 (1970) 147–157.
- [2] A.J. Kumnick, H.H. Johnson, Deep trapping states for hydrogen in deformed iron, Acta Metall. 28 (1980) 33–39.
- [3] R. Kirchheim, Interaction of hydrogen with dislocations in palladium—I. Activity and diffusivity and their phenomenological interpretation, Acta Metall. 29 (1981) 835–843.
- [4] K. Kiuchi, R.B. McLellan, The solubility and diffusivity of hydrogen in wellannealed and deformed iron, Acta Metall. 31 (1983) 961–984.
- [5] R.V. Bucur, N.O. Ersson, X.Q. Tong, Solubility and diffusivity of hydrogen in palladium and Pd₇₇Ag₂₃ containing lattice defects, J. Less Common Met. 172–174 (1991) 748–758.
- [6] G.A. Young, J.R. Scully, The diffusion and trapping of hydrogen in high purity aluminum, Acta Mater 46 (1998) 6337–6349.
- [7] H.K. Birnbaum, P. Sofronis, Hydrogen-enhanced localized plasticity—a mechanism for hydrogen-related fracture, Mater. Sci. Eng. A 176 (1994) 191–202.
- [8] R.D. Calder, T.S. Elleman, K. Verghese, Grain boundary diffusion of tritium in 304-and 316-stainless steels, J. Nucl. Mater 46 (1973) 46–52.
- [9] T. Tsuru, R.M. Latanision, Grain boundary transport of hydrogen in nickel, Scr. Metall. 16 (1982) 575–578.
- [10] S.M. Lee, J.Y. Lee, The trapping and transport phenomena of hydrogen in nickel, Metall. Trans. A 17 (1986) 181–187.
- [11] B. Ladna, H.K. Birnbaum, SIMS study of hydrogen at the surface and grain boundaries of nickel bicrystals, Acta Metall. 35 (1987) 2537–2542.
- [12] A. Kimura, H.K. Birnbaum, Hydrogen induced grain boundary fracture in high purity nickel and its alloys—enhanced hydrogen diffusion along grain boundaries, Acta Metall. 36 (1988) 757–766.
- [13] T.M. Harris, R.M. Latanision, Grain boundary diffusion of hydrogen in nickel, Metall. Trans. A 22 (1991) 351–355.
- [14] G. Palumbo, D.M. Doyle, A.M. El-Sherik, U. Erb, K.T. Aust, Intercrystalline hydrogen transport in nanocrystalline nickel, Scr. Metall. Mater 25 (1991) 679–684.
- [15] M. Ichimura, Y. Sasajima, M. Imabayashi, Grain boundary effect on diffusion of hydrogen in pure aluminum, Mater. Trans. JIM 32 (1991) 1109–1114.
- [16] D.R. Arantes, X.Y. Huang, C. Marte, R. Kirchheim, Hydrogen diffusion and permeation in micro-and nanocrystalline nickel, Acta Metall. Mater 41 (1993) 3215–3222.
- [17] A.M. Brass, A. Chanfreau, Accelerated diffusion of hydrogen along grain boundaries in nickel, Acta Mater 44 (1996) 3823–3831.
- [18] H. Natter, B. Wettmann, B. Heisel, R. Hempelmann, Hydrogen in nanocrystalline palladium, J. Alloys Compd. 253–254 (1997) 84–86.
- [19] U. Stuhr, T. Striffler, H. Wipf, H. Natter, B. Wettmann, S. Janssen, R. Hempelmann, H. Hahn, An investigation of hydrogen diffusion in nanocrystalline Pd by neutron spectroscopy, J. Alloys Compd. 253–254 (1997) 393–396.
- [20] B. Szpunar, L. Lewis, I. Swainson, U. Erb, Thermal expansion and hydrogen diffusion in nanocrystalline nickel, Phys. Rev. B 60 (1999) 10107–10113.
- [21] Y. Mine, K. Tachibana, Z. Horita, Grain-boundary diffusion and precipitate trapping of hydrogen in ultrafine-grained austenitic stainless steels processed by high-pressure torsion, Mater. Sci. Eng. A 528 (2011) 8100–8105.
- [22] W. Beck, J.O.'M. Bockris, J. McBreen, L. Nanis, Hydrogen permeation in metals

176

as a function of stress, temperature and dissolved hydrogen concentration, Proc. R. Soc. A 290 (1966) 220-235.

- [23] B. Chew, F.T. Fabling, The effect of grain boundaries on the low-temperature diffusion of hydrogen in decarburized mild steel, Met. Sci. 6 (1972) 140-142.
- [24] V.M. Sidorenko, I.I. Sidorak, Determination of diffusion characteristics of the volume and boundary components of the flow of hydrogen in polycrystalline metals, Mater. Sci. 9 (1973) 50-54.
- [25] V.M. Sidorenko, I.I. Sidorak, Boundary and volume diffusion of hydrogen in copper, nickel, and iron, Mater, Sci. 9 (1973) 372-375.
- [26] R.M. Latanision, M. Kurkela, Hydrogen permeability and diffusivity in nickel and Ni-base allovs. Corrosion 39 (1983) 174–181.
- I. Yao, I.R. Cahoon, Theoretical modeling of gain boundary diffusion of hydrogen and its effect on permeation curves, Acta Metall. Mater 39 (1991) 111 - 118
- J. Yao, J.R. Cahoon, Experimental studies of grain boundary diffusion of [28] hydrogen in metals. Acta Metall. Mater 39 (1991) 119–126.
- [29] S Heinze B Vuillemin LC Colson P Giroux D Leterg Relation between grain size and hydrogen diffusion coefficient in an industrial Pd-23% Ag alloy, Solid State Ion. 122 (1999) 51–57.
- [30] A. Pedersen, H. Jonsson, Simulations of hydrogen diffusion at grain boundaries in aluminum, Acta Mater 57 (2009) 4036–4045. [31] A. Oudriss, J. Creus, J. Bouhattate, E. Conforto, C. Berziou, C. Savall, X. Feaugas,
- Grain size and grain-boundary effects on diffusion and trapping of hydrogen in pure nickel. Acta Mater 60 (2012) 6814–6828.
- W.Y. Choo, J.Y. Lee, Thermal analysis of trapped hydrogen in pure iron, Metall. [32] Trans. A 13 (1982) 135–140
- [33] J.Y. Lee, S.M. Lee, Hydrogen trapping phenomena in metals with BCC and FCC crystal structures by the desorption thermal analysis technique. Surf. Coatings Technol. 28 (1986) 301-314.
- [34] Y. Mine, Z. Horita, Y. Murakami, Effect of high-pressure torsion on hydrogen trapping in Fe-0.01 mass% C and type 310S austenitic stainless steel, Acta Mater 58 (2010) 649-657.
- [35] T. Mütschele, R. Kirchheim, Segregation and diffusion of hydrogen in grain boundaries of palladium, Scr. Metall. 21 (1987) 135-140.
- [36] R. Kirchheim, T. Mütschele, W. Kieninger, Hydrogen in amorphous and nanocrystalline metals, Mater. Sci. Eng. 99 (1988) 457-462.
- [37] A.P. Zhilyaev, T.G. Langdon, Using high-pressure torsion for metal processing: Fundamentals and applications, Prog. Mater. Sci. 53 (2008) 893-979.
- [38] R.E. Buxbaum, A.B. Kinney, Hydrogen transport through tubular membranes of palladium-coated tantalum and niobium, Ind. Eng. Chem. Res. 35 (1996) 530-537
- [39] K. Edalati, T. Fujioka, Z. Horita, Microstructure and mechanical properties of pure Cu processed by high-pressure torsion, Mater. Sci. Eng. A 497 (2008) . 168–173.
- Y. Ito, Z. Horita, Microstructural evolution in pure aluminum processed by [40] high-pressure torsion, Mater. Sci. Eng. A 503 (2009) 32-36.
- [41] H. Iwaoka, Z. Horita, Hydrogen behavior in ultrafine-grained palladium processed by high-pressure torsion, Int. J. Hydrogen Energy 38 (2013) 14879-14886.
- [42] B.J. Kestel, Non-acid electrolyte thins many materials for TEM without causing

hydride formation, Ultramicroscopy 19 (1986) 205-212.

- [43] T. Ungár, A. Borbély, The effect of dislocation contrast on x-ray line broadening: A new approach to line profile analysis, Appl. Phys. Lett. 69 (1996) 3173-3175.
- [44] N. Boes, H. Züchner, Electrochemical methods for studying diffusion, permeation and solubility of hydrogen in metals, J. Less Common Met. 49 (1976) 223-240
- [45] R. Kirchheim, Interaction of hydrogen with dislocations in palladium-II. Interpretation of activity results by a Fermi-Dirac distribution Acta Metall 29 (1981) 845-853.
- [46] T. Zakroczymski, Adaptation of the electrochemical permeation technique for studying entry, transport and trapping of hydrogen in metals, Electrochim. Acta 51 (2006) 2261–2266.
- I. Völkl, The Gorsky effect, Ber, Bunsenges, Phys. Chem. 76 (1972) 797–805. H. Nagamoto, H. Inoue, Sorption and desorption of hydrogen on palladium [48]
- sheet, Nippon, Kagaku Kaishi 1977 (1977) 1264–1270. [49]
- H. Hasegawa, K. Nakajima, Effect of hydrogen on the mechanical properties of Pd, J. Phys. F. Metal. Phys. 9 (1979) 1035–1046. H. Katsuta, R.J. Farraro, R.B. McLellan, The diffusivity of hydrogen in palladium, [50]
- Acta Metall. 27 (1979) 1111–1114. [51] R. Kirchheim, R. McLellan, Electrochemical methods for measuring diffusiv-
- ities of hydrogen in palladium and palladium alloys, J. Electrochem. Soc. 127 (1980) 2419 - 2425.
- Y. Sakamoto, N. Tabaru, Diffusivity and solubility of hydrogen in annealed and [52] cold rolled specimens of palladium, J. Jpn. Inst. Met. 45 (1981) 1048-1055.
- [53] H. Züchner, H.G. Schöneich, Improvement of electrochemical methods for studying the diffusion and solubility of hydrogen in metals, J. Less Common Met. 101 (1984) 363-372.
- R.V. Bucur, Measurements of diffusion coefficients of hydrogen in palladium [54] by a galvanostatic permeation method, Int. J. Hydrogen Energy 10 (1985) 399-405
- [55] H. Hagi, Boundary conditions in electrochemical measurements of diffusion coefficients of hydrogen in α-palladium, Mater. Trans. JIM 31 (1990) 842-847.
- [56] T. Maeda, S. Naito, M. Yamamoto, M. Mabuchi, T. Hashino, High-temperature diffusion of hydrogen and deuterium in palladium, J. Chem. Soc. Faraday Trans. 90 (1994) 899-903.
- S. Hara, A. Caravella, M. Ishitsuka, H. Suda, M. Mukaida, K. Haraya, E. Shimano, [57] T. Tsuii. Hydrogen diffusion coefficient and mobility in palladium as a function of equilibrium pressure evaluated by permeation measurement, J. Memb. Sci. 421-422 (2012) 355-360.
- [58] C. Zener, Theory of D₀ for atomic diffusion in metals, J. Appl. Phys. 22 (1951) 372-375
- [59] R. Kirchheim, X.Y. Huang, A relationship between prefactor and activation energy for diffusion, Phys. Status Solidi 144 (1987) 253-257.
- [60] R. Kirchheim, F. Sommer, G. Schluckebier, Hydrogen in amorphous metals-I, Acta Metall. 30 (1982) 1059-1068.
- [61] Y.S. Lee, D.A. Stevenson, Hydrogen permeation in amorphous Cu-Ti and Pd-Si alloys, J. Non. Cryst. Solids 72 (1985) 249-266.
- [62] H. Gleiter, Nanocrystalline Materials, Prog. Mater. Sci. 33 (1989) 223-315.