Ion-Irradiation Effects of Hydrogen Absorption in Palladium Metal

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The effect of ion irradiation on palladium (Pd) metal was investigated by hydrogen absorption measurements and synchrotron X-ray diffraction. The N^+ irradiation was made with an acceleration energy 350 keV. The initial hydrogen absorption reaction rate of the N^+-irradiated Pd was three times larger than that of non-irradiated Pd. The microscopic structure was investigated by using the pair-distribution function (PDF) obtained by synchrotron X-ray diffraction. Although the average structure of the Pd was face-centered cubic (fcc) structure, the Pd atoms were displaced and two occupancy sites were revealed. This site occupancy is closely related with the hydrogen absorption reaction rate.

Key words: pair-distribution function, synchrotron X-ray diffraction, N^+-irradiation, hydrogen absorption, Pd

1. INTRODUCTION

Recently, several methods of an ion irradiation for hydrogen storage materials have been investigated and it was found that the ion irradiation are possible to improve the hydrogen absorption reaction rate [1]. Low energy ion irradiation is quite useful for surface modification of materials. Abe *et al.* showed that the hydrogen solubility of He^+ irradiated Pd is four times larger than that of non-irradiated one [2,3]. These studies have revealed the potential of the ion irradiation for improving the hydrogen storage materials.

The microscopic origin of the ion-irradiated Pd in general is not well understood. It is expected that the ion irradiation affects the Pd metal both on the surface modification and on the microscopic structure [4,5,6].

There have been very few reports of the structural analysis on the ion-irradiated hydrogen storage materials [7,8]. The ion-irradiated area is limited on the surface of the material even in the high-energy ion irradiation. Moreover, both the ion irradiation and hydrogen storage reaction introduce a large amount of vacancies and defects in the material. Since the ion-irradiated and hydrogen-storage material are disorder systems, the conventional crystallographic analysis cannot reveal such disorder systems.

In this paper, we present a detailed study of the local structure of ion-irradiated and non-irradiated Pd metals by high-energy synchrotron X-ray diffraction (HEXRD) and atomic pair-distribution function (PDF) [9]. The PDF technique has long been used to characterize structures of glasses, liquids, and amorphous materials and recently found its application to study local structures of disordered crystalline materials. The PDF measures the probability of finding an atom at a distance r from another atom. One of the advantages of the PDF method over other local probes such as X-ray absorption fine structure (XAFS) is that it gives both local and intermediate range information, because both Bragg peaks and diffuse scattering are used in this analysis.

2. EXPERIMENTAL

The details of sample preparation are given in Ref. 2. Essentially, the Pd sheets (99.99 % purity) with a size of 10 x 10 x 0.2 mm^3 were irradiated to one side whole with N^+ in an acceleration energy with 350 keV and a dose range of $1 \times 10^{17}/cm^2$. We have already investigated the irradiation effect of Pd metal with various ions and with various acceleration energies. The heavier the ionic species and the higher the acceleration energy, the more the hydrogen absorption reaction rate improved. However, in this study, the microstructure of Pd metal is investigated by the X-ray diffraction. When the irradiated heavy ion stays in the Pd metal, it might influence the X-ray diffraction measurements. Moreover, surface roughness of the Pd metal is changed when the irradiation energy too high, and the reflectivity of the X-rays might be change. Therefore, the ionic species and acceleration energy were decided.
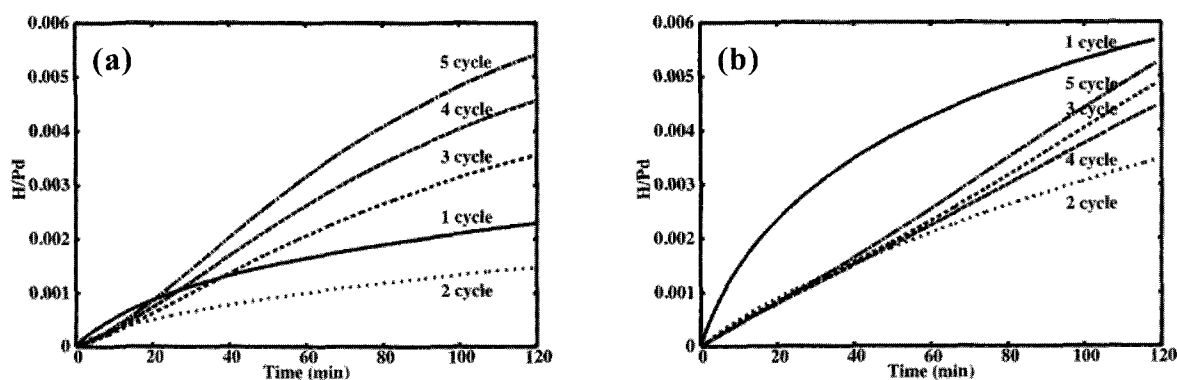
Fig. 1 Change in the ratio of absorbed hydrogen atoms to Pd atoms ([H]/[Pd]) for (a) non-irradiated and (b) N^+-irradiated Pd.

Hydrogen absorption reaction rate measurements were carried out in an electrolytic cell [10]. The Pd sheet was used as a cathode. The opposite electrode of Pt sheet was used as an anode. Hg/HgO electrode was used as the reference electrode in an open cell. The electrolyte of 6M-KOH was used for all rate measurements. In all hydrogen reaction experiments, no gas bubbles were observed during hydrogen absorption.

Optical microscopy of the sample surface, as well as scanning electron microscopy (SEM), using a JEOL-JSM-5400 scanning microscope, were utilized to check the surface morphology before X-ray measurements. There was no damage that influenced the X-ray measurements by the ion irradiation.

Synchrotron X-ray powder diffraction data were collected at room temperature with 30 keV X-rays at BL14B1 of SPring-8, which is a bending-magnet beamline dedicated to Japan Atomic Energy Agency. Scattered radiation was collected with reflection geometry. By combining the selected energy and the reflection geometry, the scatterers contain the information of only the ion-irradiated area.

3. RESULTS

3.1 Hydrogen absorption reaction measurement

Figures 1(a) and (b) show the results of hydrogen absorption reaction rate in the non-irradiated and N^+-irradiated Pd, as a function of time. All measurements were performed at room temperature in the atomosphic pressure. The hydrogen reaction rate can be determined from a temporal change in the [H]/[Pd] value. In the non-irradiated Pd, the hydrogen absorption reaction rate of the initial stage was [H]/[Pd] = 0.0022 at the reaction time was 120 min. The hydrogen absorption reaction rate was reduced in the second charge, and then increased step by step. Finally, the 5-cycles hydride of the [H]/[Pd] was 0.0054, which was the twice the initial stage. On the other hand, the hydrogen absorption reaction rate of the N^+-irradiated Pd of the initial stage was [H]/[Pd] = 0.0056, which was also twice the initial stage of the non-irradiated Pd. The hydrogen reaction rate was reduced in the 2-cycles, then increased gradually and finally the 5-cycles of the [H]/[Pd] was 0.0052, which was as much as the initial stage of the N^+-irradiated Pd.
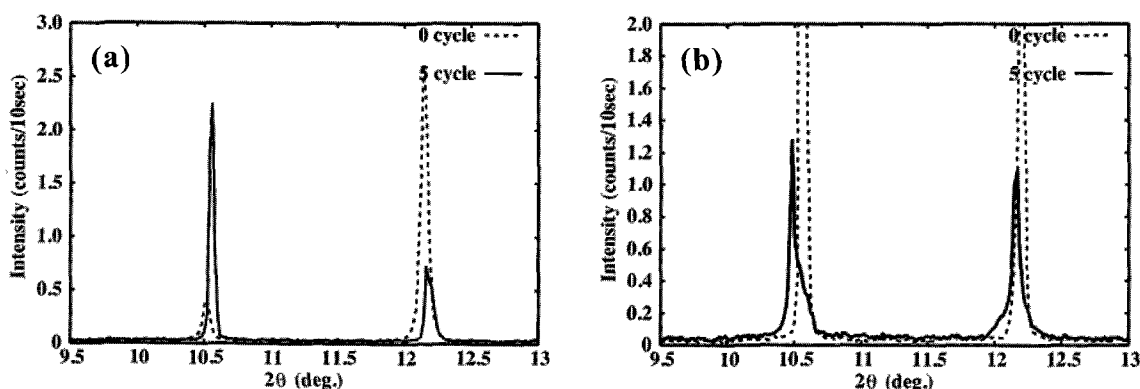

Fig. 2 X-ray diffraction profiles of (a) non-irradiated and (b) N^+-irradiated Pd around (111) and (200) Bragg peaks. The profiles were measured before hydride (dashed lines) and after 5-cycles hydride (solid lines).

3.2 X-ray diffraction

Figures 2 (a) and (b) show the X-ray diffraction patterns of the non-irradiated and N^+-irradiated Pd around (111) and (200) Bragg peaks. In the non-irradiated Pd, the observed peak intensity was changed through hydriding process, but the widths of the Bragg peaks remained sharp. In the N^+-irradiated Pd, the intensity of the Bragg peaks were reduced drastically in the 5-cycles hydride and the widths of the 5-cycles hydride Pd were much broader than those of the non-hydride Pd. This peak broadening indicates that somewhat disorder structure was introduced in the N^+-irradiated Pd. In Fig. 2(b), the Bragg peaks of the samples with 5-cycles hydride were shifted to lower position. Since the Pd sheets were stretched during the rolling process, the lattice parameters of the Pd sheets before hydride were larger than those of the normal bulk Pd. This strain was reduced by the ion irradiation and the hydrogen absorption. As a result, the lattice parameters of Pd sheets were also reduced and the Bragg peaks shifted to lower angle. Similar behavior was also reported in Ref. 7.

3.3 PDF analysis

The sample dependent single scattering, $S(Q)$, was obtained using standard procedures [11,12]. The data were corrected for absorption, multiple scattering, and polarization effects. Background and Compton scattering were removed and the data were normalized for flux and number of scatterers. It should be noted that this is a high value of the wave vector for the HEXRD measurement; for comparison Q_{max} achieved with a conventional source such a Cu anode is less than 8 $\mathring{A}^{-1}$. In this work, the upper limit of $Q_{max} = 18$ $\mathring{A}^{-1}$ was used. The experimental PDF, $G(r)$, is obtained by taking the Fourier transform of the reduced structure factor $S(Q)$, according to the following equation:

$$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1]sin(Qr)dQ \quad (1).$$

The resulting PDFs of the non-irradiated Pd before hydride and the N^+-irradiated Pd after 5-cycles hydride

are shown in Figs. 3 (a) and (b), respectively. Since the Pd metals are fcc structure, the nearest-neighbor peak appears around $2.6 \sim 2.8$ $\mathring{A}$. The peaks those exist less than 2.4 $\mathring{A}$ are the ghost peaks by Fourier termination errors. The PDF peaks of these samples are located at almost the same position. The difference was only observed in the nearest-neighbor PDF peak.

Figure 4(a) shows the $G(r)$s around the nearest-neighbor peak of the non-irradiated Pd before the hydride and after the 1- and 5-cycles hydride. Before the hydride, the nearest-neighbor peak shows a singlet peak at 2.8 $\mathring{A}$. In the 1-cycle hydride Pd, the nearest-neighbor peak split in two peaks. The main peak located at 2.8 $\mathring{A}$ reduced compare to the 0-cycle hydride, instead, the new peak appeared at the 2.6 $\mathring{A}$. In the 5-cycles hydride Pd, the longer peak continued to reduce and the shorter peak increased. In the N^+-irradiated Pd, the shorter 2.6-$\mathring{A}$-peak appeared in the non-hydride Pd and the longer 2.8-$\mathring{A}$-peak appeared in the 1-cycle hydride Pd, as shown in Fig 4(b). Except for these peaks, a broad peak existed at the center of these peaks in the 5-cycles hydride Pd.

4. DISCUSSION

The nearest-neighbor peak position has a relationship with the hydrogen absorption reaction rate. Compare to the hydrogen absorption reaction rate measurements of the non-irradiated Pd (Fig. 1(a)), the hydrogen absorption reaction rate is low, when the nearest-neighbor peak is located at 2.8 $\mathring{A}$ (before hydride) and it is high when the peak is located at 2.6 $\mathring{A}$ (5-cycles hydride). The hydrogen absorption reaction rate increased with changing the atomic position from 2.8 $\mathring{A}$ to 2.6 $\mathring{A}$. We speculated that the shift of atomic position originated from the vacancy that is introduced by the hydriding process. The shorter atomic position of 2.6 $\mathring{A}$ should indicate a high-density vacancy state. Similar behavior was also seen in the N^+-irradiated Pd. When the nearest-neighbor peak located at the shorter 2.6 $\mathring{A}$ (0-cycle sample), the hydrogen absorption reaction rate is high, because the vacancy was introduced by the N^+ irradiation. After the 1-cycle hydride, the vacancy site of the N^+ irradiation should be
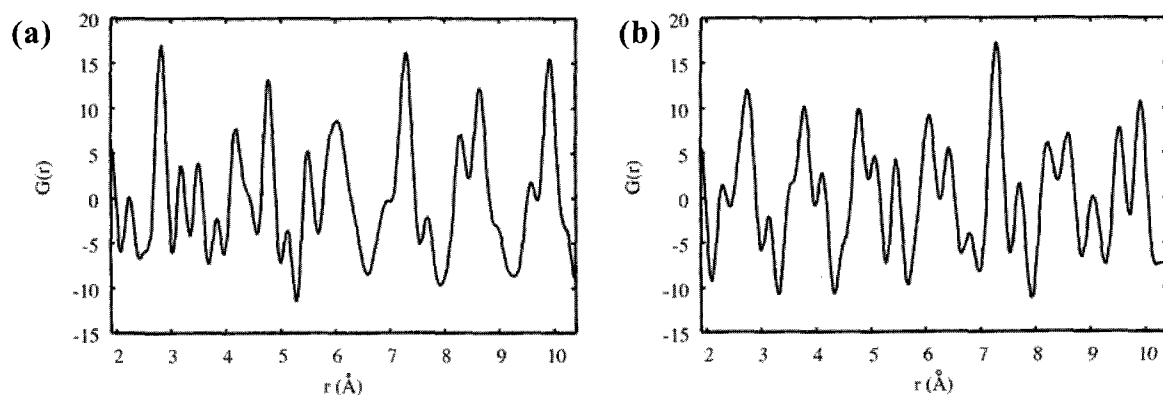

Fig. 3 (a) Real-space bond distribution obtained by X-ray PDF for the non-irradiated Pd and non-hydride Pd. (b) Real-space bond distribution for the N^+ irradiated Pd and 5-cycles hydride one.

driven away by the hydriding-introduced vacancies. The peak broadening of the 5-cycles hydride Pd is caused by the conflict between the ion-irradiation introduced vacancies and the hydriding-introduced vacancies.

We now address the 1-cycle hydride in the N^+-irradiated Pd. Although the hydrogen absorption reaction rate of the N^+-irradiated Pd was improved, the 2-cycles hydrogen absorption reaction rate was reduced drastically, as shown in Fig. 1(b). It seems somewhat different behavior occurred before the 2-cycles hydride. The change in the hydrogen storage capacity is reflected in the local structure. Before the 2-cycles hydride, the nearest-neighbor peak position of the N^+-irradiated sample was shifted to the low-hydrogen absorption state of the longer 2.8-Å-bond distance, as shown in Fig. 4(b). The hydrogen absorption reaction rate tended to recovery after the 2-cycles hydride.

The hydrogen storage capacity was improved by the N^+-irradiation (except 2-cycles hydride). We checked that this tendency maintained to the hydriding cycle of the 20 times. However, the local structure was disordered by the N^+ irradiation and the hydriding processes. The atomic displacement might bring the pulverization of Pd making forward.

4. SUMMARY

The effects of N^+ irradiation in the hydrogen-storage Pd metal by hydrogen absorption reaction rate measurements and X-ray diffraction. We clarified that the two atomic positions existed in the Pd depending on the vacancy condition. The longer and shorter atomic distances indicated the local environments of the high- and low-hydrogen absorption reaction states, respectively. The N^+-irradiated Pd showed the disorder feature due to the conflict of the vacancies introduced by the ion irradiation and the hydride.

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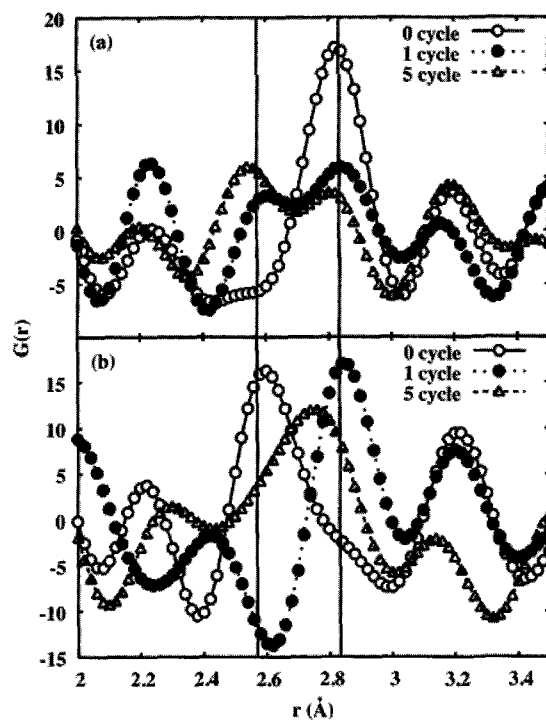
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Fig. 4 The experimental PDFs of (a) non-irradiated and (b) N^+-irradiated Pd sheets around the nearest-neighbor distance.

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