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In situ measurement of lattice parameter change on Pd and Ni during cathodic hydrogen charging

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Abstract

A device for in situ X-ray diffraction measurements during cathodic hydrogen charging has been developed. The lattice change on Pd before and after hydrogen charging has been clearly demonstrated. The results of $\Delta a/a$ for Pd and Ni during increasing hydrogen concentration have been shown. The device is effective for understanding metal–hydrogen systems under various constrained hydrogen environments. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In many metals, lattice parameter increases by dissolving hydrogen atoms. The concentration of hydrogen C_H is estimated by a relation, $\Delta a/a = 1/3C_H V_H/\Omega$, where Ω is the atomic volume of a metal and V_H the volume of a hydrogen atom and is about 2.8 \AA^3 for most metals, which is summarized in Refs. [1,2]. Pd–H system is well investigated by means of XRD [3–6]. However, most experiments were performed in two-phase (α and β) co-existing region, in which the interaction of hydrogen atoms with the matrix atoms may be more complicated. Therefore, experiments under lower C_H region are required. Lattice expansion due to hydrogen storage in Ni has been investigated by Baranowski and co-workers [7,8]. They have also measured for many fcc metals and alloys.

Most common measurements of lattice parameters for cathodically hydrogen charged metals have been carried out in the condition of after-charging. In this condition, as the concentration of hydrogen atoms may decrease by diffusion or the Gorski effect, measurements concern with surviving or equilibrium hydrogen atoms. Therefore, in situ measurements under the hydrogen environment are expected to be worthwhile for the understanding of dynamic behavior of activated hydrogen atoms. One of the

other problems for the measurements using polycrystalline samples is the precision of the measurements. The precision of lattice parameter change by common measurements using a polycrystal is order of 10^{-3} – 10^{-4} . The value corresponds to the concentration of hydrogen atoms of bigger than 10^{-2} – 10^{-3} , which may cause the change of the feature by introduced dislocations or cracks. Therefore, lower concentration is required.

In the present work, we have developed a device for high-precision in situ measurements on cathodically hydrogen-charged metals.

2. Experimental

A device for in situ X-ray diffraction measurements during cathodic hydrogen charging has been developed. A schematic figure is shown in Fig. 1. Aqueous solution of 1 N H_2SO_4 flows through on the surface of a sample. The thickness of the solution flow was 0.3 mm and the velocity is 0–80 mm/s. It is mounted on a goniometer, therefore, easy and precise set-up can be realized. In this condition, the decreasing of the diffracted X-rays is about 50% compared with that without solution. Cathodic hydrogen charging was performed at room temperature and the charging current was 1–100 mA/cm² and the total charge was up to 30 Coulomb for Pd and 300 Coulomb for Ni, respectively. The stability of charging current was ± 0.1 mA. The uniform flow was confirmed by the flow of small visible bubble produced by charging of 100 mA. A Rigaku

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Mylar window

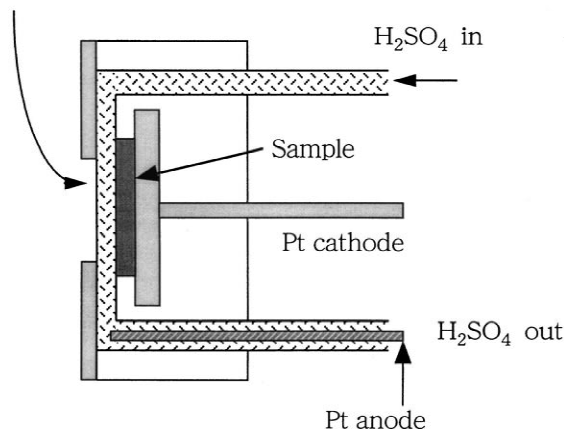


Fig. 1. A cell for cathodic hydrogen charging.

X-ray generator was used for the experiment. Cu K α was employed with the condition: 50 kV and 10–300 mA. $\omega-2\theta$ step scan mode was adopted with a step of 2θ of 0.01 or 0.02°. The measuring time for a 2θ point was 1–10 s. A HOPG crystal was used as an analyzer monochromator. Intensities of uncharged samples in the solution were about 3000 cps with 50 kV and 10 mA operation. The experimental set-up is shown in Fig. 2. Although FWHM of line profiles due to the divergence of incoming X-rays from an uncharged sample was 0.12° in our experiment, the peak position was recognized within $\pm 0.002^\circ$ by fitting, which corresponds to $\pm 1 \times 10^{-5}$ in $\Delta a/a$. Polycrystals of Pd and Ni ($8 \times 8 \times 0.2$ mm³) were annealed in vacuum at 1323 K for 1 h and 750 K for 2 h, respectively. Small single-crystal grains obtained by the treatment were examined. (420) and (400) reflection were adopted for Pd and Ni, respectively.

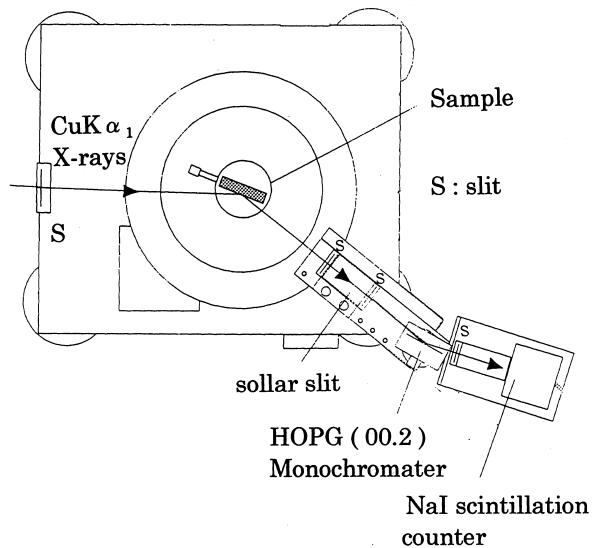


Fig. 2. XRD system for the experiment.

3. Results

Fig. 2 shows the effect of current on–off to the lattice expansion of Pd. The right scale C_H is the estimated hydrogen concentration by the relation, $\Delta a/a = 1/3 C_H V_H / \Omega$. Cathodic hydrogen charging started with 1 mA/cm² (point a) for 20 min and stopped for 20 min (point b). Discontinuous increase of the lattice parameter, $\Delta a/a = 0.41 \times 10^{-4}$, was observed just after charging, it decreased to 0.32×10^{-4} by current off. With the charging current of 2 mA/cm² (point c), $\Delta a/a$ increased by 1.30×10^{-4} up to 1.52×10^{-4} , and decreased to 1.24×10^{-4} on stopping the charging (point d). Further charging started with 4 mA/cm² (point e) and brought on an immediate change: $\Delta a/a = 3.27 \times 10^{-4}$. The lattice expansion increased up to 1.65×10^{-3} at 80 C/cm² and gradually decreased by further charging (Fig. 3). The dose dependence of the intensity is shown in Fig. 4. It began to decrease rapidly at 20 C charging. The intensity over 60 C charging is about 2% of the initial intensity.

In the case of Ni, a large charging current of 100 mA/cm² was adopted. The lattice parameter increased up to 2.4×10^{-4} and decreased to that of uncharged (Fig. 5). The maximum C_H was 2.8×10^{-3} . The intensity also decreased by charging (Fig. 6).

3.1. Discussion

The diffusion coefficient of hydrogen D in Pd at room temperature is known to be 2×10^{-7} cm²/s (see also Ref. [1]). The average migration distance of hydrogen atoms r for 1 s is estimated as about 6 μ m by the relation: $r \sim (2Dt)^{1/2}$. A total of $4 \times 6.24 \times 10^{15}$ hydrogen atoms is supplied into a volume $1 \times 1 \times 0.0006$ cm³/s when the implantation current is 4 mA/cm². Hence, the number of H atoms N_H in 1 cm³ is 4.2×10^{22} , assuming the implantation efficiency 100%. The number of Pd atoms in 1 cm⁻³

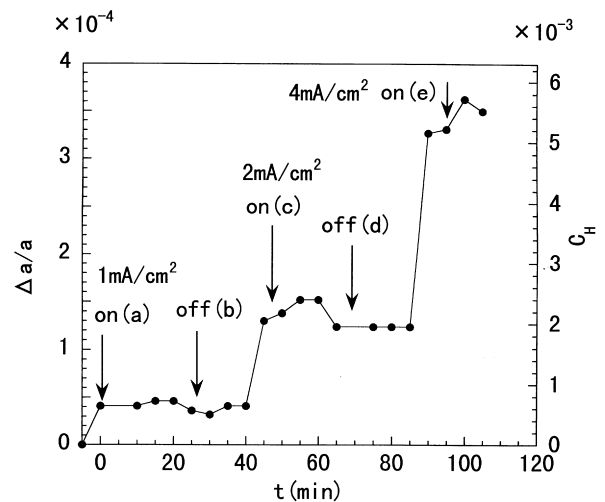


Fig. 3. Lattice parameter change by charging current on–off.

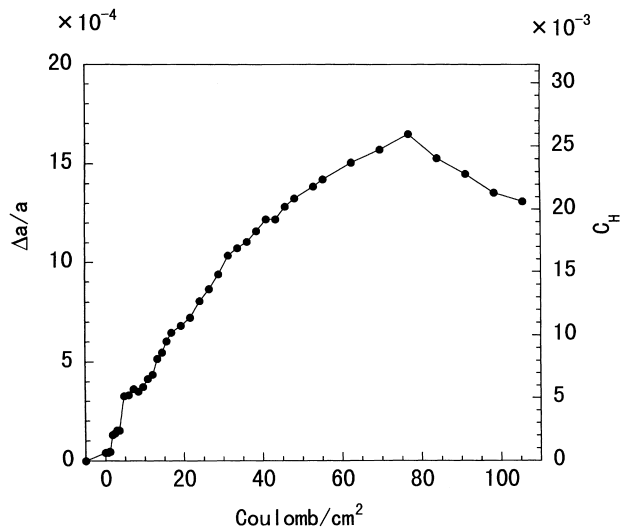


Fig. 4. Hydrogen dose dependence of lattice parameter for Pd.

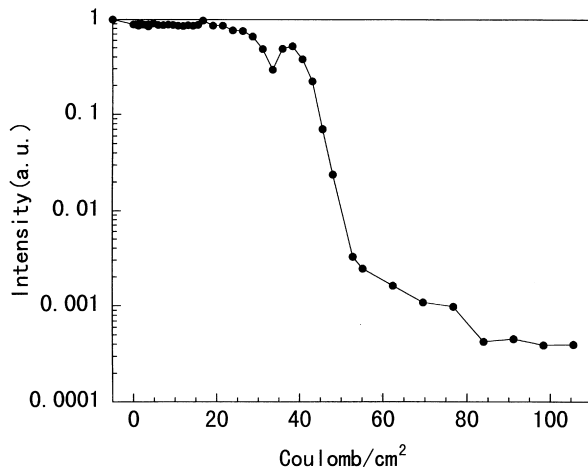


Fig. 5. Hydrogen dose dependence of intensity for Pd.

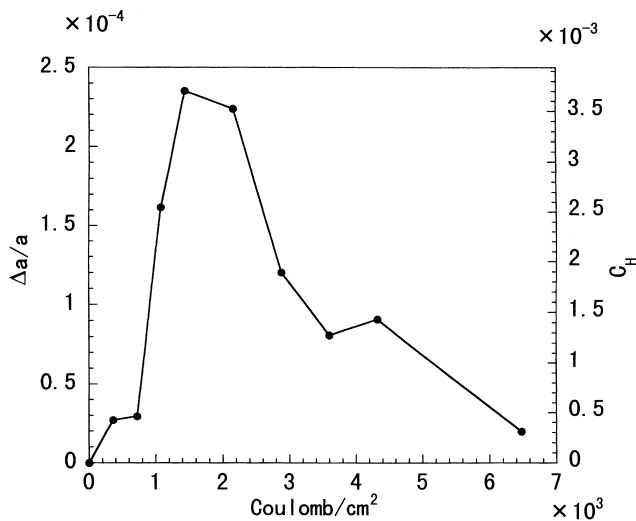


Fig. 6. Hydrogen dose dependence of lattice parameter for Ni.

N_{Pd} is $4 \times (3.88 \times 10^{-8})^{-3}$ and is 6.8×10^{22} . In this case, the concentration of hydrogen $C_H N_H / N_{Pd}$ is estimated as 6.1×10^{-4} . The measured C_H increase at point e is 3.2×10^{-3} adopting $V_H = 2.8^3$ during 100 s of the measurement. Therefore, the implantation efficiency is estimated as 5%. C_H at 80 C/cm^2 charging is estimated as 0.026. The increase of $\Delta a/a$ below 80 C/cm^2 is considered to be the lattice expansion due to dissolved hydrogen atoms and the decrease above that due to the formation of the hydride phase (phase) [9], which is suggested by the intensity decrease beginning at the 20-C charging. The intensity decrease corresponds to the increase of the volume fraction of phase and also caused by the polycrystallization of phase, which disperse in the crystal orientation. Since phase itself and the grain boundaries introduced by the transformation may act as sinks of hydrogen atoms, C_H in α phase is considered to be decreased.

The maximum C_H in Ni is 2.4×10^{-4} , which is much lower compared with that in Pd, and is the same order compared with calculation [10]. The reason is that the higher chemical potential of hydrogen in Ni leads to lower implantation efficiency and smaller $\Delta a/a$. The decrease of lattice parameter over 1200 C may due to NiH hydride formation, which was not confirmed in this experiment.

3.2. Summary

The device used in our experiments is compact, easy to set-up and can be mounted on a conventional goniometer head. The precision in $\Delta a/a$ is $\pm 1 \times 10^{-5}$. In situ measurement is important since the behavior of activated H atoms into a matrix metal gives the dynamic interaction in metal-hydrogen systems.

For Pd, rapid response of lattice parameter change by current on-off was clearly observed. The change is consistent with that estimated by calculation. Maximum C_H and subsequent decrease are related to the formation of hydride.

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