

New determination method of hydrogen diffusivity in titanium-hydrides by means of diffraction-enhanced X-ray imaging method

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The X-ray refraction imaging technique, diffraction-enhanced X-ray imaging (DEI) method was applied to determine the hydrogen diffusivity in titanium-hydride. Hydride was formed on titanium surface by electrolytic-charging at room temperature for 6, 12, 18, 24 and 48 h. The specimen was cut into a 1-mm thick slice for cross-sectional observation. Hydride layer was observed by DEI method as a thick black or white line parallel to the surface. Hydride distribution caused by hydrogen diffusion from the surface was calculated using assumed hydrogen diffusivity and a solution of diffusion equation. And the results were converted to the intensity profile of refraction images of the hydride using the measured rocking curve from an analyzer. The intensity profile was compared with that obtained from the photographs and fitted diffusivity was decided by trial and error. The obtained diffusion coefficient of hydrogen in titanium-hydride, $3.6 \times 10^{-15} \text{ m}^2/\text{s}$, was slightly larger than the value obtained by internal friction at room temperature.

Key words: diffusion, hydrogen, titanium-hydride, diffraction-enhanced X-ray imaging

1. INTRODUCTION

Considerable efforts have been made toward to investigate the interaction between hydrogen and metals in order to develop hydrogen-storage materials etc. In consequence, much knowledge was acquired. For example, in the titanium containing higher concentration of hydrogen, titanium atoms span a slightly tetragonally distorted face centered tetragonal lattice and hydrogen atoms occupied tetrahedral interstitial sites [1, 2]. In the study of diffusion of hydrogen in the titanium, Wipf et al. determined the diffusion coefficient of hydrogen in titanium and have reported that the activation energy of diffusion was 0.49 eV [3]. However, these investigations deal less commonly or indirect detecting techniques, such as nuclear magnetic resonance (NMR) or mechanical spectroscopy study and so on. It is necessary to establish the commonly detected technique of hydrogen or hydride in metals for investigations of metal-hydride system.

An imaging technique with high-energy X-ray is an important diagnostic tool. Contact radiography and tomography using high-energy X-rays provide information on internal structure that cannot be obtained using other non-destructive method. In conventional imaging techniques utilizing high-energy X-rays, X-rays that pass through an object along different paths are differently absorbed, and the intensity pattern of the emerging beam records the distribution of absorbing materials within the specimen. In generally, difference between the absorption coefficient of metal and its hydride is negligible small. Therefore, it is impossible to visualize the hydride in matrix metal. However, there is another technique in X-ray imaging called phase-contrast imaging or refraction-contrast imaging [4]. Such an approach offers improved contrast sensitivity, especially when imaging

weakly absorbing specimens [5]. This technique, refraction contrast X-ray microscopy, has been successfully used and is seeing excellent and rapid progress as a diagnostic tool in medicine, biology and material sciences, because of the application of a highly parallel X-ray beam provided by synchrotron radiation source [6-8]. Although the difference in refraction indexes between titanium and titanium-hydride is extremely small, about 10^{-8} for 30keV X-ray, we were able to visualize a high-contrast projection image of the hydride using refraction-contrast radiography [9]. Most suitable refraction radiography for material sciences is diffraction-enhanced X-ray imaging method because it is easy to separate the refraction images and absorption images in an X-ray photograph taken by the imaging method. In this method, two photographs are taken with different but small offset angles of the analyzer crystal, which are the high-angle side and low-angle side images of the rocking curve. The contrast of the image originating from refraction was switched between the two photographs. As mentioned above, the techniques were widely used for the biological samples, so almost all investigation was limited the qualitative observation. Few quantitative studies such as determination of the physical constant were reported. Therefore, we applied the diffraction-enhanced X-ray imaging technique to visualize hydride formed by an electrolytic-charge with different charging times on α -titanium surface and evaluated the diffusion coefficient of hydrogen.

2. EXPERIMENTAL PROCEDURES

Polycrystals of α -titanium (99.99 at. %) supplied by Sumitomo Titanium Co. Ltd were used for specimens in the present investigation. The specimen's dimensions were approximately 1.0 x 5 x 15 mm or 1.0 x 3 x 15 mm.

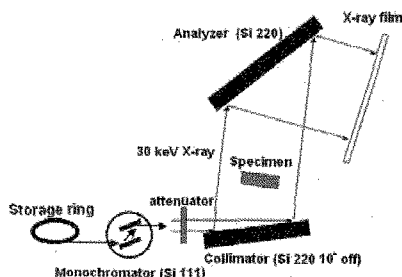


Fig. 1 Schematic diagram of the beam line and experimental setup for diffraction-enhanced X-ray imaging method.

The specimens were annealed at 800 °C for 1 hour under ultrahigh vacuum before hydrogen charging. To observe a cross section of specimens, we prepared specimens with hydride deposited on the surface by an electrolytic-charge. The charge was carried out in 1-N sulfuric acid at room temperature. Electrolytic-charging times and current density were 6, 12, 18, 24 and 48 hours and 5 mA/mm², respectively. The specimen was cut into a 1-mm thick slice for cross-sectional observation.

The present observations were performed at a vertical-wiggler beam line, BL-14B (precision X-ray optical station), at the Photon Factory in the High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. A schematic experimental setup for X-ray diffraction-enhanced imaging method is shown in Fig. 1. The X-ray energy was tuned to 10 keV by the beam line monochromator. However, 10keV X-ray (fundamental wave) was attenuated by 1 mm thick aluminum plate and 30 keV X-ray (third harmonics) was used for observation. The collimator and the analyzer were cut from a silicon ingot, and their surfaces were mechano-chemically polished to remove defects and strains. The collimator was adjusted at the asymmetric 220-diffraction condition. The angle between the crystal surface and the reflecting plane was 10°. The analyzer was adjusted close to the symmetric 220-diffraction condition. The distance between specimen and film was about 0.5 m. The exposure time for all refraction images was 2 - 3 min. Images were stored on mammographic

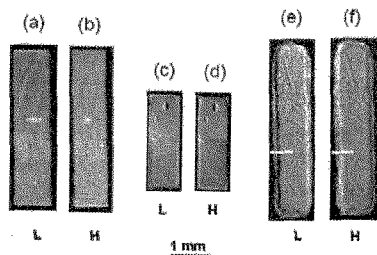


Fig. 3 Diffraction-enhanced images of the cross-section of the specimens taken by 30 keV X-ray. The images (a), (b) are before the electrolytic-charging. The images (c), (d) are after 18 h charging. The images (e), (f) are after 48 h charging. The marks L and H shows taken at low-angle and high-angle side images of the rocking curve.

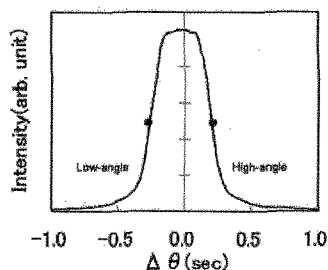


Fig. 2 Measured rocking curve of the analyzer for the transmitted X-rays from the specimen. We recorded the diffracted X-rays from the analyzer on an X-ray film at each offset angle of $\Delta\theta$ shown as closed circles.

film (Kodak Min-R 2000) with a spatial resolution of about $10 \times 10 \mu\text{m}^2$.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The rocking curve of the analyzer for the transmitted X-rays from the specimen was measured and is shown in Fig.2. We recorded the diffracted X-rays from the analyzer on an X-ray film at each offset angle of $\Delta\theta$ from the Bragg condition shown as closed circles in Fig.2. These two photographs show low-angle ($\Delta\theta = -0.25^\circ$) and high-angle ($\Delta\theta = 0.20^\circ$) side images of the rocking curve. Figure 3 shows diffraction-enhanced images of the cross-section of titanium-hydride specimens before (a), (b) and after the electrolytic-charging (c) ~ (f). The low- and high-angle images are shown in Fig. 3 (a), (c), (e) and 3 (b), (d), (f), respectively. Electrolytic-charging time of (c), (d) and (e), (f) was 18 and 48 hours, respectively. There is no hydride observed in Fig.3 (a), (b). The circumference of the specimen shows white and black contrast images and the image is reversed between Fig. 3 (c) and 3 (d) or 3 (e) and 3 (f) similar to previously reported results [9]. Because hydrogen charging of this specimen was carried out at room temperature, hydrogen atoms could not diffuse into the crystal so fast on account of the high migration energy of hydrogen (0.49 eV). [3] Thus, hydrides were formed on the near surface of the specimen. Figure 4 shows intensity distribution along

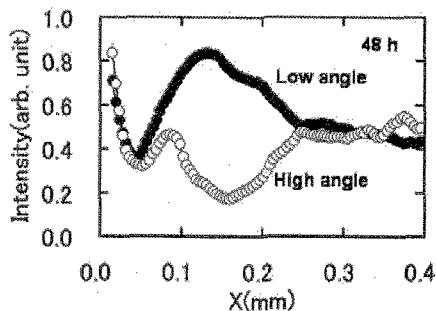


Fig. 4 Intensity distribution of Fig. 3(e) and 3(f) toward inside from the surface. The full and open circles indicate intensity of low-angle side image, Fig. 3 (e), and high-angle side one, Fig. 3 (f), respectively.

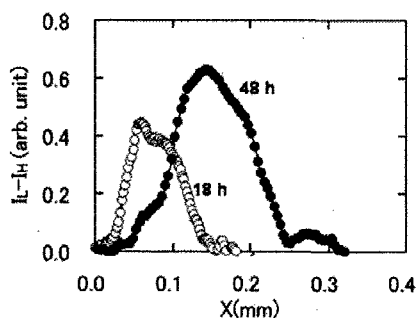


Fig. 5 The net intensity profiles of refracted X-ray beam of specimen. Open and full circles indicate the intensity profile after 18 h and 48 h charging, respectively.

the black thin line from the surface of 48 h charged specimens shown in Fig. 3 (e) and (f). The full and open circle in Fig. 4 indicates intensity of low-angle side image, Fig. 3 (e), and high-angle side one, Fig. 3 (f), respectively. However, these intensity profiles contain absorption effect by the specimen. In order to exclude absorption, we introduce the net X-ray intensity of refracted beam, ΔI ,

$$\Delta I = I_L - I_H, \quad (1)$$

where I_L and I_H are intensity of low-angle image and high-angle image shown in Fig. 4, respectively. Intensity profile, ΔI , of 18 and 48 h charged specimens is shown in Fig. 5.

In order to determine the diffusion coefficient of hydrogen atom in titanium-hydride, we compare the above results and calculated intensity profile of refracted X-ray by hydride in titanium. Intensity profile is estimated from the hydrogen concentration in titanium. In the titanium-hydrogen system, heats of solution of hydrogen into titanium and formation energy of hydride, TiH_2 , are both negative.[10] So, the hydride formation is controlled by diffusion process of hydrogen atom in the hydride. We first calculated the hydrogen distribution using a solution of one-dimensional diffusion equation. In the present experiment, surface concentration of hydrogen was held at constant during the electrolytic

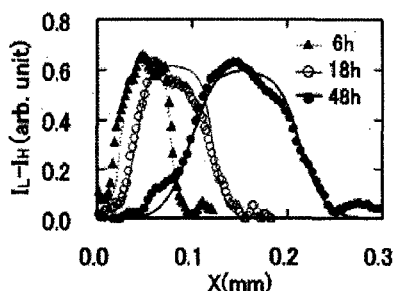


Fig. 7 Calculated intensity profile of refracted X-ray and observed one. Triangles, open and full circles indicate after 6h, 18 h and 48 h charging, respectively. Solid lines indicate observed intensity profile shown in Fig.5.

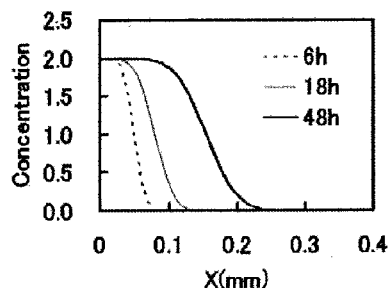


Fig. 6 Calculated normalized hydrogen distribution.

Open and full circles indicate after 18 h and 48 h charging, respectively.

charging. Therefore, the normalized hydrogen concentration c/c_0 is expressed by Shewmon as follows,[11]

$$\frac{C}{C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2),$$

where $\operatorname{erf}(x)$ is referred to as the complementary error function, c is the concentration of hydrogen, t is the charging time, x is the space coordinate measured normal to the specimen's surface and D is the diffusion coefficient. The calculated normalized hydrogen distributions using the assumed diffusion coefficient, $D=3.3 \times 10^{-15} \text{ m}^2/\text{s}$, for 6, 18 and 48h are shown in Fig.6. In the figure, broken line, thick line and thin line indicate the diffusion profile of hydrogen after 6, 18 h and 48 h charging, respectively. We regarded that the distribution of hydride was the same as that of diffused hydrogen atoms because of the negative value of formation energy of hydride. Furthermore, distribution of the real part of the refractive index in the crystal was obtained from the ratio of hydride and titanium. The real part of refraction index of hydride and titanium for 30 keV X-ray is $1-1.01 \times 10^{-6}$ and $1-9.7 \times 10^{-7}$, respectively [12]. Next, deviation angle of X-ray by refraction was calculated from density distribution of hydride using velocity of light in the specimen and Snell's law. Furthermore, X-ray intensity was calculated from the deviation angle using the rocking curve shown in Fig. 2. Finally, estimated X-ray intensity was compared with the net X-ray intensity, ΔI , obtained from the photograph. We supposed the diffusivity of a hydrogen atom in the above calculations and determine the optimum diffusivity by the trial and error. The fittest calculated intensity profile of 6, 18 and 48 h charging specimens and observed one are shown in Fig. 7. The agreement between the measured curves of X-ray intensity profile and calculated one provides the strong evidence that this technique is a very useful tool for investigation of diffusion process. The obtained diffusion coefficients of hydrogen in titanium-hydride are plotted as the charging-time in Fig. 8 and average diffusion coefficient was $3.6 \times 10^{-15} \text{ m}^2/\text{s}$. In spite of macroscopic measurements, the obtained values of hydrogen diffusivity from the above method showed good agreement. However, the diffusion coefficients are slightly larger than the widely accepted value at room temperature.[3,10] The reason is explained by the assumption that the specimen temperature rose by reactions and

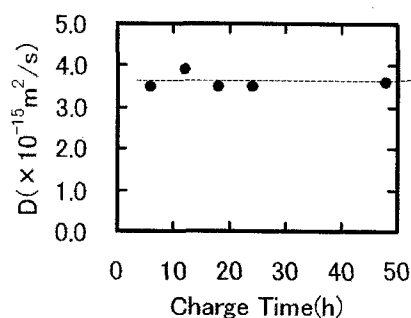


Fig. 8 Diffusion coefficients of hydrogen in titanium-hydride for different charging time.

Joule heating during the electrolytic charging. If we accumulate the similar data at different temperature, the activation energy and pre-exponential factor of hydrogen diffusion can be obtained. This diffraction-enhanced imaging method appears to be a promising new technique for not only non-destructive inspection but also investigation of diffusion process in materials sciences.

4. ACKNOWLEDGMENTS

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