Transaction of the Materials Research Society of Japan 34[2] 229-232 (2009)

Distribution of Hydride in Titanium Determined by X-Ray Diffraction-Enhanced Imaging Method with Asymmetric Reflection Analyzer

Kaoru Mizuno, Takashi Kanai*, Kei-ichi Hirano** and Hiroyuki Okamoto***
Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan
FAX: 81-852-32-6404, e-mail: mizuno@riko.shimane-u.ac.jp
* Faculty of Science, Kanazawa University, Kanazawa 920-1192, Japan
FAX: 81-76-234-4360, e-mail: kanai0904@gmail.com
** High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan
FAX: 81-29-864-2801, e-mail: keiichi.hirano@kek.jp
*** Faculty of Medicine, Kanazawa University, Kanazawa 920-0942, Japan
FAX: 81-76-234-4360, e-mail: okamoto@mhs.mp.kanazawa-u.ac.jp

The X-ray refraction imaging technique, diffraction-enhanced X-ray imaging (DEI) method with an asymmetric reflection analyzer was applied to determine the distribution profile of hydride in titanium. Horizontal magnification of the image by the asymmetric reflection was 9 times. Hydride was formed on titanium surface by electrolytic-charging at room temperature for 10, 25.5, 48 and 150 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. X-ray intensity profile of hydride was measured from the DEI image and converted to the deviation angle of X-ray by refraction using the observed rocking curve. The distribution of refraction index was calculated from the deviation angle of X-ray using Snell's low. Finally distribution of ratio of hydride and titanium, the concentration profile of hydride, was obtained from that of the refraction index. The distribution profile of hydride in titanium was determined to accuracy of the order of micrometer by means of the DEI method with asymmetric reflection analyzer.

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

1. INTRODUCTION

Many investigations have been made on the interaction between metals and hydrogen atoms in order to solve problems such as hydrogen embrittlement in steel or hydrogen-storing materials. 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 hydride 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. A few studies on direct observation of hydride in metals by electron microscopy have been reported; however, this observation was limited to only local areas and conditions [4]. 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 [5]. Such an approach offers improved contrast sensitivity, especially when imaging weakly absorbing specimens [6]. 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 [7-9]. 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 [10]. Most suitable refraction radiography for material sciences is diffraction-enhanced X-ray imaging [DEI] 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

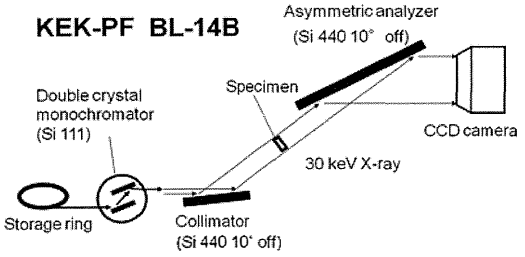

Fig. 1 Schematic diagram of the beam line and experimental setup for diffraction-enhanced X-ray imaging method.

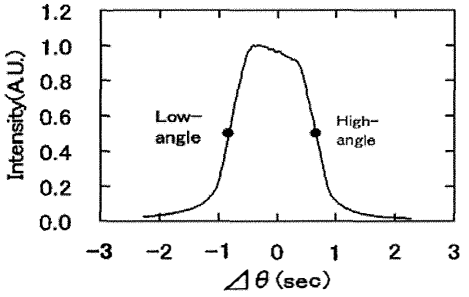

Fig. 2 Measured rocking curve of the analyzer for the transmitted X-rays from the specimen. We recorded the diffracted X-rays from the analyzer on an X-ray film at each offset angle of $\Delta\theta$ shown as closed circles.

times on α-titanium surface and evaluated the diffusion coefficient of hydrogen [11]. However, observations were limited for specimens with thick hydride layer (>100μm) because of its low-resolution power. Therefore, we applied the X-ray DEI method with asymmetrical reflection analyzer for magnification of layer images of hydride and determined the distribution of hydride in titanium.

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^3.

The specimens were annealed at 800 ℃ 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 63 ℃. Electrolytic-charging times and current density were 10, 25.5, 48 and 150 hours and 5 mA/mm^2, 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 30 keV by the beam line monochromator. 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 440-diffraction condition. The angle between the crystal surface and the reflecting plane was 10°. The analyzer was adjusted close to the asymmetric 440-diffraction condition. The angle between the crystal surface and the reflecting plane for asymmetric reflection was 10° (asymmetric ratio: 0.112). Horizontal magnification of the image by the asymmetric reflection was 9 times. The distance between specimen and film was about 0.5 m. The exposure time of CCD-camera was about 20 s.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The rocking curve of the asymmetric reflection 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 a CCD-camera at each offset angle of $\Delta\theta$ from the Bragg condition shown as closed circles in Fig.2. These two photographs show low-angle ($\Delta\theta$ = -0.80") and high-angle ($\Delta\theta$ = 0.65") side images of the rocking curve. Figure 3 shows diffraction-enhanced images of the cross-section of titanium-hydride specimens using the asymmetric reflection (a), (b) and the previous symmetric reflection analyzer (c), (d). The low- and high-angle images are shown in Fig. 3 (a), (c) and 3 (b), (d), respectively. Although the height of images in Fig. 3 is the same, width of Fig. 3 (a) and (b) is 9 times as great as that of (c) and (d). Electrolytic-charging time of the specimen was 25.5 hours. There is hydride observed in Fig.3. The circumference of the specimen

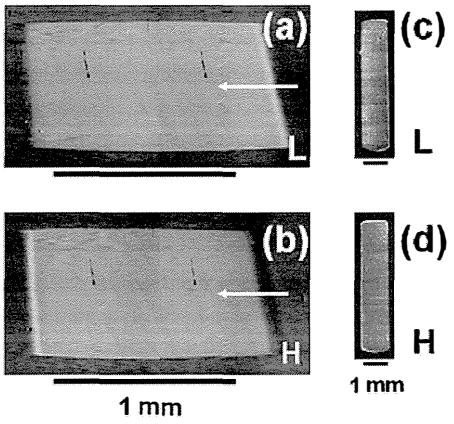

Fig. 3 Diffraction-enhanced images of the cross-section of the specimens taken by 30 keV X-ray. The images (a), (b) are taken using the asymmetric reflection analyzer. The images (c), (d) are under the symmetric reflection. The marks L and H shows taken at low-angle and high-angle side images of the rocking curve.

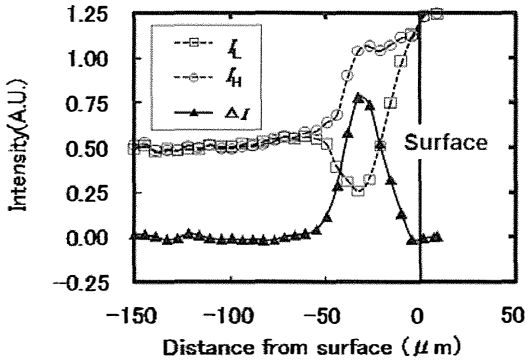

Fig. 4 Intensity distribution of Fig. 3(a) and 3(b) toward inside from the surface. The squares and circles indicate intensity of low-angle side image, Fig. 3 (a), and high-angle side one, Fig. 3 (b), respectively. The triangles indicate the net intensity profiles of refracted X-ray beam of specimen.

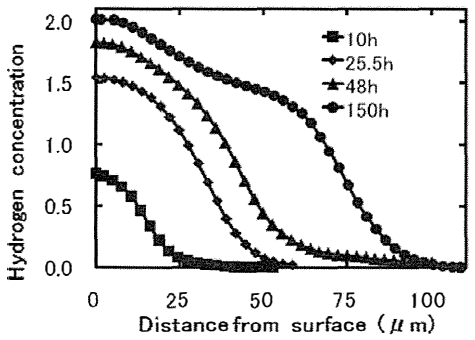

Fig. 5 The hydrogen concentration vs. distance from the specimen surface. High concentration region of hydrogen was moved toward the inner area of the specimen according to the charging time.

shows white and black contrast images and the image is reversed between Fig. 3 (a) and 3 (b) or 3 (c) and 3 (d) similar to previously reported results [10]. Because hydrogen charging of this specimen was carried out at 63 ℃, 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 the white thin arrow from the surface of 25.5 h charged specimens shown in Fig. 3 (a) and (b). The square and circle in Fig. 4 indicate intensity of low-angle side image, Fig. 3 (a), and high-angle side one, Fig. 3 (b), 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,

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

where I_H and I_L are intensity of high-angle image and low-angle image shown in Fig. 4, respectively. Intensity profile, ΔI, of 25.5 h charged specimens is shown in Fig. 4 as triangles.

In order to determine the distribution of hydride in titanium, we obtained the deviation angle of X-ray by refraction from intensity profile, ΔI, using the rocking curve shown in Fig. 2. Next, the distribution of refraction index was calculated from the deviation angle of X-ray using Snell's low. Finally distribution of ratio of hydride and titanium, the concentration profile of hydride, was obtained from that of the refraction index. The real part of refraction index of hydride and titanium for 30 keV X-ray is $1\text{-}1.01\times10^{-6}$ and $1\text{-}9.7\times10^{-7}$, respectively [12].

The obtained concentration profile of hydride of 10, 25.5, 48 and 150 h charging specimens were shown in Fig.5. In the titanium-hydrogen system, heat solution of hydrogen into titanium and formation energy of hydride,TiH_2, are both negative [13]. Hydrogen atoms in the titanium immediately formed hydride. So we can consider the concentration profile of hydride as distribution of hydrogen as shown in Fig.5.

Figure 5 shows the hydrogen concentration vs. distance from the specimen surface. High concentration region of hydrogen was moved toward the inner area of the specimen according to the charging time. The concentration profile of hydrogen in titanium was determined to accuracy of the order of micrometer by means of the asymmetric reflection analyzer. In spite of convenient means, the obtained results of hydrogen concentration from the present method showed the improvement of spatial resolution. However, use of the asymmetric reflection analyzer reduces the resolution power of angle [14]. This magnification method has limitations. The diffraction-enhanced imaging method with the asymmetric reflection analyzer appears to be a promising new technique for not only non-destructive inspection but also investigation of micro-process in materials sciences.

4. ACKNOWLEDGMENTS

This work has been performed under the approval of the Photon Factory Advisory Committee (Proposal No. 2008G544). We also thank Sumitomo Titanium Co. Ltd for supplying high purity titanium crystals.

5. REFERENCES

[1] L. D. Bustard and R. M. Cotts: Phys. Rev. B**22** 12-17 (1980).
[2] E. Zuzek,J. P. Abriata, A. San-Martin, F. D. Manchester: Bull. Alloy Phase Diagr. **11** 385-391 (1990).
[3] H. Wipf, B. Kappesser and R. Werner: J. Alloys and Compounds **310**190-197 (2000).

[4] K. Aoyagi, E. P. Torres, T. Suda, S. Ohnuki: J. Nuclear Materials **283-287** 876 (2000).
[5] V. A. Somenkov, A. K. Tkalch and S. Sh. Shil'shtein: Sov. Phys. Tech. Phys. **36** 1309 (1991).
[6] J. Kirz: Q. Rev. Biophys., **28** 33-39 (1995) .
[7] A. Snigirev, I. Snigreva, V. Kohn, S. Kuzunetsov and I. Schelokov: Rev. Sci. Instrum. **66** 5486-5490 (1995).
[8] N. Yagi, Y. Suzuki, K. Umetani, Y. Kohmura and K. Yamasaki: Med. Phys. **26** 2190-2195 (1999).
[9] K. Kagoshima, Y. Tsusaka, K. Yokoyama, K. Takai, S. Takeda and J. Matsui: Jpn. J. Appl. Phys. **38** L470-L474 (1999).
[10] K. Mizuno, T. Kobayashi, F. Fujiki, H. Okamoto, Y. Furuya, K. Hirano: J. Alloys and Compounds **402** 109-115 (2005).
[11] K. Mizuno, Y. Furuya, K. Hirano and H. Okamoto: Physics Status Solidi (a) **204** 2734-2739 (2007).
[12] http://www-cxro.lbl.gov
[13] Y. Fukai: The Metal-Hydrogen System (Springer Verlag, New York, 1993), Chap.1, p. 38.
[14] A. Authier: Dynamical Theory of X-ray Diffraction (Oxford Univ. Press, New York, 2001) p.107.

(Received December 25, 2008; Accepted March 3, 2009)