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Direct Observation of Hydride Formed in Pure Titanium by Refraction-Enhanced X-ray Imaging Method

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We apply the refraction-enhanced imaging technique using extremely parallel X-ray beams from a so-called third generation synchrotron radiation source such as SPring-8 to observe titanium polycrystals containing titanium-hydride. Although the hydride in titanium cannot be observed by conventional radiography that utilizes absorption of X-rays, we visualized a high-contrast projection image of hydride using refraction-contrast radiography. This is a promising new technique for non-destructive inspection in bulk material systems with only small differences between refraction indexes.
Key words: X-ray refraction imaging, phase contrast, synchrotron radiation, titanium hydride

1. INTRODUCTION

Considerable efforts have been applied toward investigating the interaction between metals and hydrogen atoms in order to solve problems such as hydrogen embrittlement in steel or hydrogen-storing materials. However, many investigations in metal physics deal with indirect detection techniques for hydrogen such as thermal desorption or penetration of hydrogen atoms. 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.[1] As yet there have been no reports on direct observation of shape, distribution, formation and decomposition of hydride in bulk metals under highly concentrated hydrogen atmospheres. Although titanium and its alloys are promising materials for preserving hydrogen, until now it has been impossible to visualize the hydride in titanium with non-destructive methods.

Imaging techniques utilizing high-energy X-rays such as projection radiography and tomography, have been used for many years to non-destructively observe the image contrast of the internal structures of objects in material science, biology and medicine.[2] In conventional radiography, 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 sample. An alternative approach is phase-contrast radiography, which instead records variations in the phase of the emerging radiation.[3] Such an approach offers improved contrast sensitivity, especially when imaging weakly absorbing samples.[4] This technique, phase contrast X-ray microscopy, is successfully progressing now in the soft X-ray region because of application for diagnostic tools in medicine and biological X-ray microscope.[5] For imaging in the hard X-ray region, a extreme parallelism is needed in order to enhance the contrast and to be able to resolve phase variations across the beam. Because of the extremely parallel X-ray beam provided by a third-generation synchrotron radiation source such as SPring-8, it is possible to realize phase-contrast imaging directly from the sample in transmission geometry.[6-8] Therefore, this work has been planned with the aim of confirming the visualization of titanium-hydride in titanium by the refraction-enhanced X-ray imaging method.[9]

2. EXPERIMENTAL PROCEDURES

The specimens used in this investigation were polycrystals of titanium (99.99 at. %). The sample's dimensions were approximately 1.0 x 10 x 20 mm. After annealing at 600°C in a vacuum for 1 hour, a specimen was annealed at 560°C in hydrogen gas at 1 atm, and the annealing time was 66 min. for formation of titanium hydride in the specimen. To observe a cross section of specimen, we also prepared another specimen with hydride deposited on the surface by an electro-chemical charge. The charge was carried out in a mixture of perchloric acid and methyl alcohol at the ratio of 1:4 by volume at room temperature. The current density was 0.5 mA/cm^2 for 20 hours. The specimen was

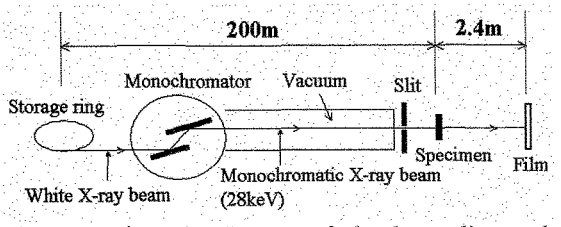

Fig. 1 Schematic diagram of the beam line and experimental setup for refraction-enhanced X-ray imaging method. The experiment was performed at beam line BL20B2 (Bio-medical imaging station) of SPring-8.

cut into a 1-mm thick slice for cross-section observation. After observation the cross-section, we annealed the specimen at 550°C in a vacuum for 1 hour in order to decompose the hydride on the surface, and observed it again.

Present experiment was performed at beamline BL20B2 (Bio-medical imaging station) of SPring-8. Schematic diagram of the beam line and experimental setup is shown in Figure 1. The X-ray energy used in this experiment was 28 keV. According to ability and stability of the monochromator, this X-ray energy was selected. The images were recorded with a long specimen-to-detector distance (2.8 m) for the refraction images in addition to a short distance (40 mm) for the absorption images. The exposure time was 20 - 30 sec. Images were stored on manmographic film (Kodak Min-R 2000) with a spatial resolution of about 10μm.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows refraction-enhanced imaging photographs of titanium without (a) and with hydride (b) taken with a long specimen-to-detector distance (2.8 m). The annealing times in hydrogen gas of the specimens shown in Fig. 2(a) and (b) were 0 (non-annealing) and 66 min, respectively. Large cracks, indicated by arrows, marked by rolling are clearly discernible in Fig. 2. These surface cracks were also observed through an optical microscope as shown in later (Fig.4). The images obtained using the refraction-enhanced imaging technique is sensitive to the presence of air in the specimen because of the large difference between the refractive indexes of titanium and air. In addition to the crack images, there are areas of weak contrast, seen in the images as white feathers in Fig. 2(b), but we could not observe the weak white contrast seen in Fig. 2(a). Then, we founded that the white contrast image originated by refraction of hydride and the images were not observed in the specimen annealed in vacuum.

Figure 3 shows an X-ray image of the hydrogen-annealed specimen shown in Fig. 2 (b) taken under absorption contrast conditions with a short specimen-to-detector distance (40 mm). In this image, we could not observe the weak white contrast seen in Fig. 2(b). This result indicates that the weak white contrast image is due to the refraction of X-rays by the hydride in specimen.

To determine that the origin of the contrast is located inside the specimen, not on the surface, the specimen was observed through an optical microscope.

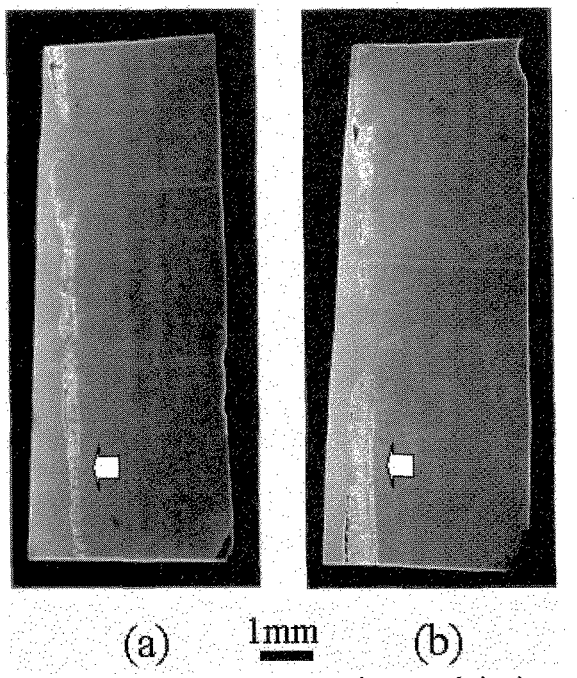

Fig. 2 X-ray refraction-contrast images of titanium specimen annealed in a vacuum (a) and hydrogen gas (b). Large cracks are indicated by arrows.

Figure 4(a) and (b) show the front and the back of the microscopic photographs of the specimen shown in Fig. 2, respectively. The feather-like images shown in Fig. 2(b) were not observed in the photographs taken through the optical microscope. Therefore, the above results provide strong evidence that the weak white contrast image shown in Fig. 2(b) results from the refraction of X-ray by the hydride formed in titanium crystal.

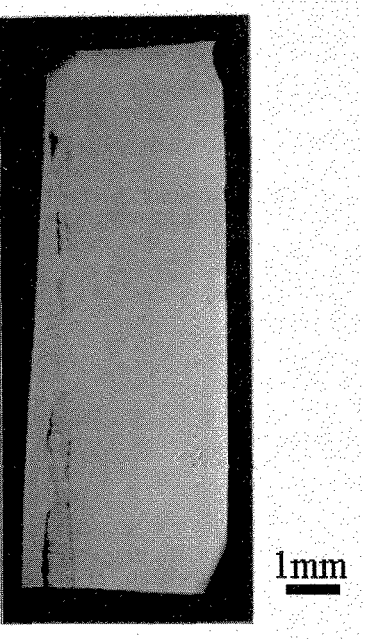

Fig. 3 X-ray absorption image of the hydrogen-annealed titanium at distance 40 mm.

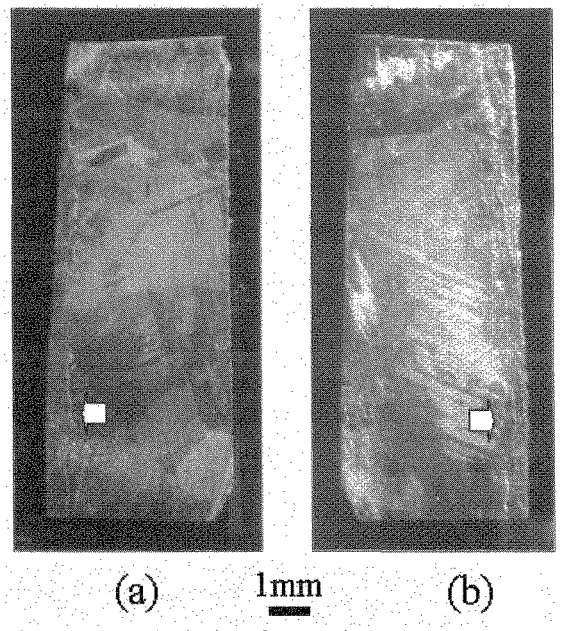

Fig. 4 Optical microscopic images of the hydrogen-annealed titanium. Arrows indicate cracks.

However, it is difficult to explicate the observed images of hydride by refraction; the hydrides have complicated shapes because they were formed by the hydrogen-gas annealing at high temperature (560°C).

To confirm that the image does indeed show the hydride in titanium, we also observed a cross-section of the specimen covered with surface hydride. Figure 5(a) shows a cross-sectional profile of the specimen charged by the electro-chemical method described above. The circumference of the specimen has white and black contrast images. Because the hydrogen-charge of this specimen was carried out at room temperature, in

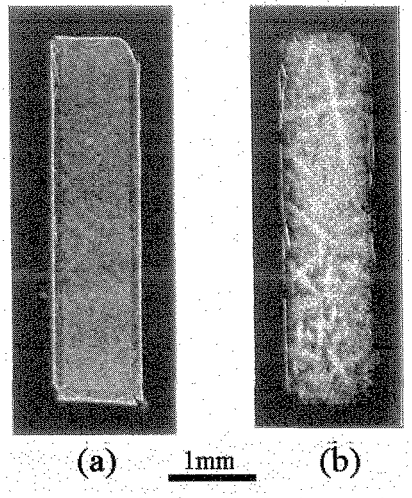

Fig. 5 X-ray refraction-contrast images through a cross-section of titanium charged by an electro-chemical method; (a) was taken after the hydrogen charge; (b) was taken after annealing at 500 ℃ in a vacuum to decompose the hydride.

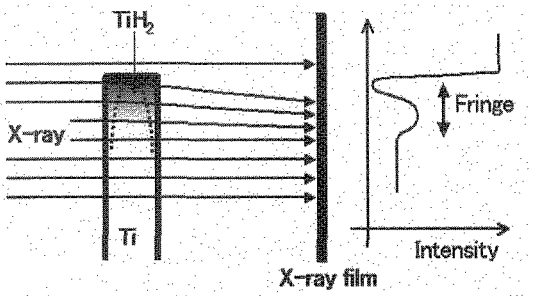

Fig. 6 Schematic view of generation of refraction contrast. The direction of the X-ray is slightly deflected at the interface.

contrast with the hydrogen gas annealing, hydrogen atoms could not diffuse into the crystal on account of high migration energy of hydrogen (0.49eV), thus hydride was formed at the surface of the specimen.[10]

The principle of generating the refraction-contrast in Fig. 5(a) is schematically shown in Fig. 6. Since the refraction index of titanium for X-rays is greater than that of titanium hydride, the distribution of titanium acts as a converging lens. Note that the direction of deflection is not the same as that for visible light because the index of refraction for X-rays is slightly smaller than unity. In this figure, the inward deflection causes a white and black fringe at the edge of the specimen as shown in X-ray intensity distribution. In Fig. 5(a), width of white band in the fringe was about one third of that of the black band. This may be attributed to that the inward deflection angle is varied by the concentration of hydride. Width of the fringe may vary according to the specimen -to-film distance. However, we could not take another photograph with difference distance in the present experiment. After X-ray observation, this specimen was annealed at 500°C for 60 min in a vacuum. The annealing is to decompose the hydride into hydrogen and titanium metal. Figure 5(b) shows a cross-sectional profile of the annealed specimen, where we can clearly observe the inner structures such as lattice defects, as opposed to Fig. 5(a), where we cannot. However, most of the refraction contrast image of hydride at the specimen surface shown in Fig. 5 (a) disappeared. Almost all the hydrogen atoms decomposed from hydride may desorb from the specimen during vacuum annealing but small amount of the atoms diffuse into the crystal lattice. They will be trapped at strain field of lattice defects and formed hydride near defects again. The hydride enhanced image contrast of defect as shown in Fig. 5(b).

In summary, we confirmed that titanium-hydride in titanium can be visualized by an X-ray refraction-enhanced imaging technique despite the small difference between refraction indexes. This refraction-enhanced imaging appears to be a promising new technology for non-destructive inspection of bulk materials.

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References

[1] K. Aoyagi, E. P. Torres, T. Suda, S. Ohnuki: J. Nuclear Materials **283-287** 876 (2000).
[2] L.V. Azaroff, B. Kaplow, N. Kato, P. Weiss, W. Wilson and S. Young: *X-ray Diffraction*, (McGraw-Hill, Sydney, 1974) pp. 180.
[3] V. A. Somenkov, A. K. Tkalch and S. Sh. Shil'shtein: Aov. Phys. Tech. Phys. **36** 1309 (1991).
[4] J. Kirz: Q. Rev. Biophys., **28** 33 (1995).
[5] A. Snigirev, I. Snigreva, V. Kohn, S. Kuzunetsov and I. Schelokov: Rev. Sci. Instrum. **66** 5486 (1995).
[6] D. C. Chapman, W. Thomlinson, R. E. Johnston, D. Washburn, E. Pisano, N. Gmur, Z. Zhang, R. Menk, F. Arfel and D. Sayers: Phys. Med. Biol. **42** 2015 (1997).
[7] K. Kagoshima, Y. Tsusaka, K. Yokoyama, K. Takai, S. Takeda and J. Matsui: Jpn. J. Appl. Phys. **38** L470 (1999).
[8] T. Weitkamp, M. Drakopoulos, W. Leitenberger, C. Raven, C. Schroer, A. Simionovici and A. Snigirev: *X-RAY MICROSCOPY*, edited by W. Meyer-Ilse, T. Warwick and A. Attwood, (American Institute of Physics, New York, 2000) pp.424.
[9] N. Yagi, Y. Suzuki, K. Umetani, Y. Kohmura and K. Yamasaki: Med. Phys. **26** 2190 (1999).
[10] H. Wipf, B. Kappesser and R. Werner: J. Alloys and Compounds **310** 190 (2000).

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