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In-situ Observation of Hydride Stability of Vanadium Alloys in Electron Microscope

S. Ohnuki*, K. Takase, K. Yashiki, K. Hamada, T. Suda and S. Watanabe
Division of Materials Science, Graduate School of Engineering,
Hokkaido University, Sapporo, 060-8278, Japan
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ABSTRACT

High-resolution microscopy was applied for surveying hydride stability in Vanadium alloys, which are candidate for hydrogen storage materials of advanced hydrogen energy systems. V_2H hydride in V alloys was stable at room temperature under the vacuum condition, but it was decomposed during heating up to 100°C. It was confirmed from HRTEM image and FFT that V_2H has a BCT structure, where hydrogen atoms locate at octahedral sites. Crystal orientation was <110>beta//<110>mat., and lattice strain is about 10%. After the decomposition of the hydride, relatively large lattice expansion was observed in the matrix, which suggests that hydrogen atoms should be trapped by lattice defects and included in the matrix. Intensive electron beam also enhanced the decomposition.

Key words : FFT, HRTEM, Hydride stability

INTRODUCTION

V-Cr-Ti alloys with body centered cubic structure have a potential for using practical hydrogen-storage alloys, because of high hydrogen storage capacity (Cho et al., 1999; Okada et al., 2002; Tamura et al., 2003). However, the hydrogen capacity strongly depends on the composition and fabrication methods, which means that lattice defects can influence the hydrogen behavior, as well as solute atoms. In V-Cr-Ti alloys we know two types of hydrides; VH_2 and V_2H (Reilly & Wiswall, 1970; Fujita et al., 1979), depending on hydrogen concentration and temperature. The former is main compound for hydrogen storage behavior, but the later is the hydride can be formed at low hydrogen pressure side and relatively stable. Mechanisms of absorption and desorption are also impotent.

Materials issues of V-Cr-Ti alloys for increasing hydrogen storage capacity are to reducing solubility limit and decreasing remained hydride, which means that the stability of hydrides are important. From these reason, high resolution electron microscopy (HRTEM) and "in-situ" observation were carried out to clarify the structure of hydride and interface as well as hydride stability.

MATERIALS AND METHODS

High purity vanadium sample was provided from National Institute of Fusion Science. The sample has full-annealed structure due to final heat-treatment at 1,100°C. Hydrogenation was carried out for 3 mm disks under 0.1 MPa of H_2 gas condition at 400°C to RT, where nominal content of hydrogen was estimated to be about 1 at%. TEM samples were electro-polished by conventional twin-jet method in H_2SO_4+ethanol solution.

For high resolution microscopy, we used VEM of 1.25 MeV installed at Hokkaido University. Furies function transfer (FFT), inverse Furies function transfer (IFFT) and Mac TEMPUS were used for structural an-

* Correspondence should be addressed to Dr. S. Ohnuki, Division of Materials Science, Graduate School of Engineering, Hokkaido University, Sapporo, 060-8278, Japan.

alysis and calculation of diffraction and images. In-situ heating experiment was carried out in the HVEM to clarify the hydride stability up to 100°C, where a digital video system used for recording images. After video-capture we applied FFT and IFFT to get detailed data on plane distance and rotation.

RESULTS AND DISCUSSION

1. Structural analysis of hydride

Fig. 1 shows HREM, FFT and IFFT images from typical area including both of V matrix and a hydride precipitate (PPT) which locates at edge-on condition. The lattice planes with about 1 nm extend to <110> direction, which means <110>beta//<110>mat. But the interface between PPT and matrix was distorted, which direction is parallel to <110> in the matrix.

Fig. 2 shows a simple crystal model for beta-hydride (V_2H) of bct structure, one of which is (010) view and other is (100) view, where lattice was expanded by 10% along to c-axis for simulating the structure. Large balls are V atom and small ones are hydrogen atoms which locate at octa-headral sites, where the total structure is an ordered phase. By using the crystal model, we calculated diffraction pattern as shown in Fig. 1. It is well

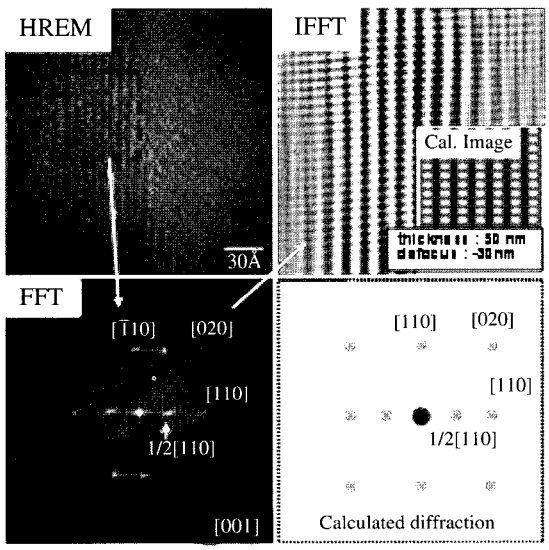

Fig. 1. High resolution image of hydride precipitate (V_2H) and calculated image from simple crystal; model.

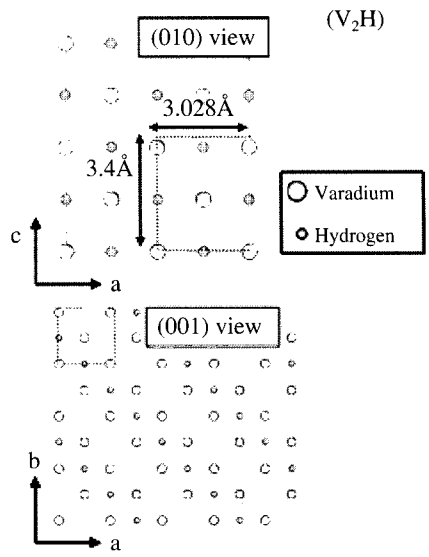

Fig. 2. Simple crystal model embedded hydrogen atoms in BCT structure.

consisted with FFT from actual PPT in basically, for example, 1/2 (110) spots are reproduced by the calculated pattern. But, comparing in the detail, we could realize some distortion occurred in the actual PPT, see FFT in Fig. 1.

Fig. 3 shows the interface structure between bcc matrix and hydride. By using FFT/IFFT, we can confirm that the structure contains large amount of strain along <110> directions. The incoherent interface should include plain defects and dislocations, which were observed in the photographs. Fig. 4 shows the model of diffraction spots from V matrix (white circles) and hydride precipitate (dark circles). The crystallographic relation is not ideal, and the distortion occurred in diffraction pattern are more than in the model, which showing un-isotropic strain.

2. Macroscopic in-situ observation

No structural change of the hydride was observed in a vacuum condition of the microscope at RT. Fig. 5 shows the continuous observation of hydride structure under intensive electron beam: 1.25 MeV HVEM at RT, where the hydride was decomposed during e-irradiation. The decomposition was so quick within 80 sec, which means it may be an irradiation-enhanced process. After

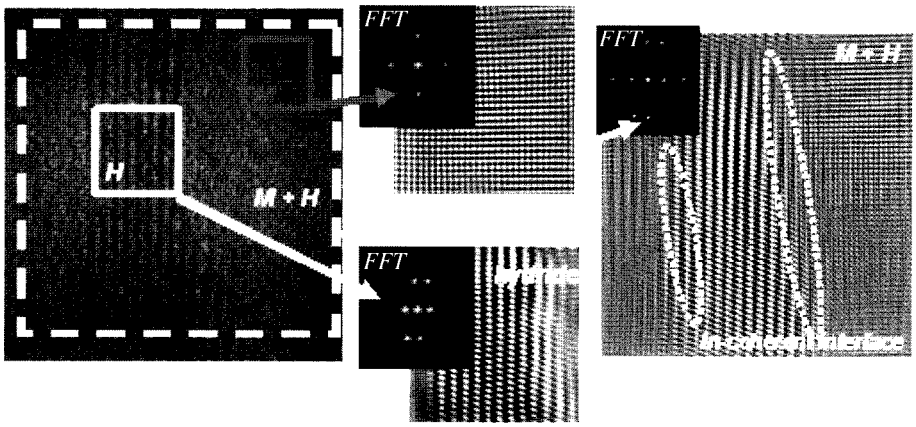

Fig. 3. Lattice image, FFT and IFFT from hydride and matrix. Large distortion can be observed at the interface.

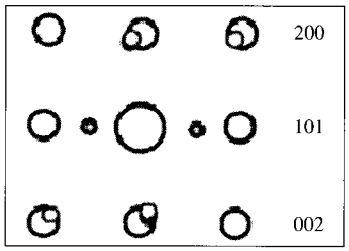

Fig. 4. SADP of $<100>$ from hydride and matrix, which is showing the rotation to $<110>$.

the decomposition, defect clusters (dislocation loops) were developed, which suggested many factors, for example, H trapping by defect clusters, high energy particle collision, dissolution and enhanced-diffusion.

3. Hydride decomposition

Fig. 6 shows in-situ observation of hydride decomposition during heating at 100°C, where the high resolution electron microscopy (HREM) was carried out from the direction of $<111>$. They were recorded in digital VTR system. Images are composed of wide and narrow lattices, but distorted partially which consist with the local strain. FFT which equivalent with selected area diffraction pattern indicates this area is beta-hydride of bct structure. With heating the decomposition progressed quickly, and the structure turned to bcc within 2 min, as shown in FFT. However, some lattice defects remained in the bcc structure, as shown in the circle, which is assumed to be dislocations.

Fig. 7 shows the sets of lattice images from FFT and

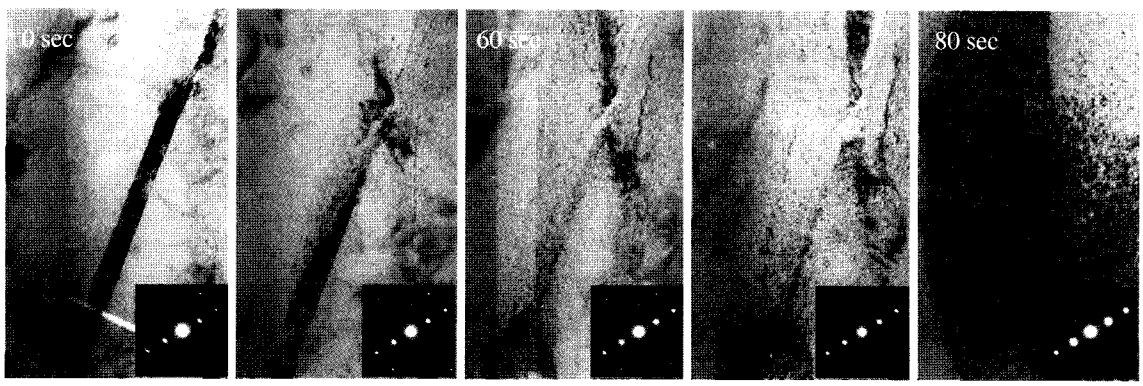

Fig. 5. disappearing hydride and developing radiation damage during observation with intensive beam at room temperature.

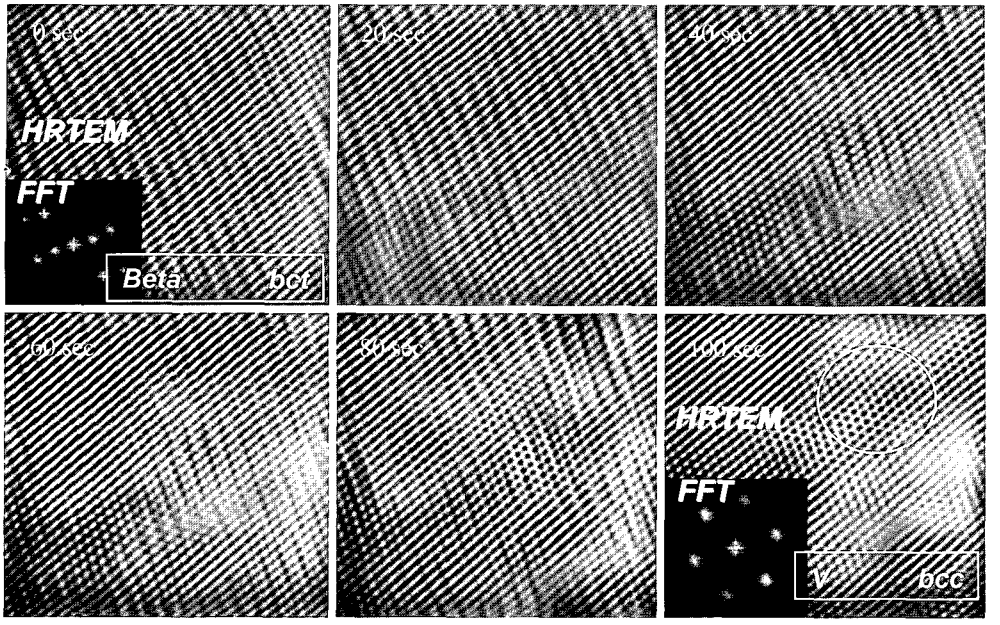

Fig. 6. Lattice image and FFT during heating observation at 100°C. The hydride of V_2H was decomposed and return to BCC lattice up to 100 sec.

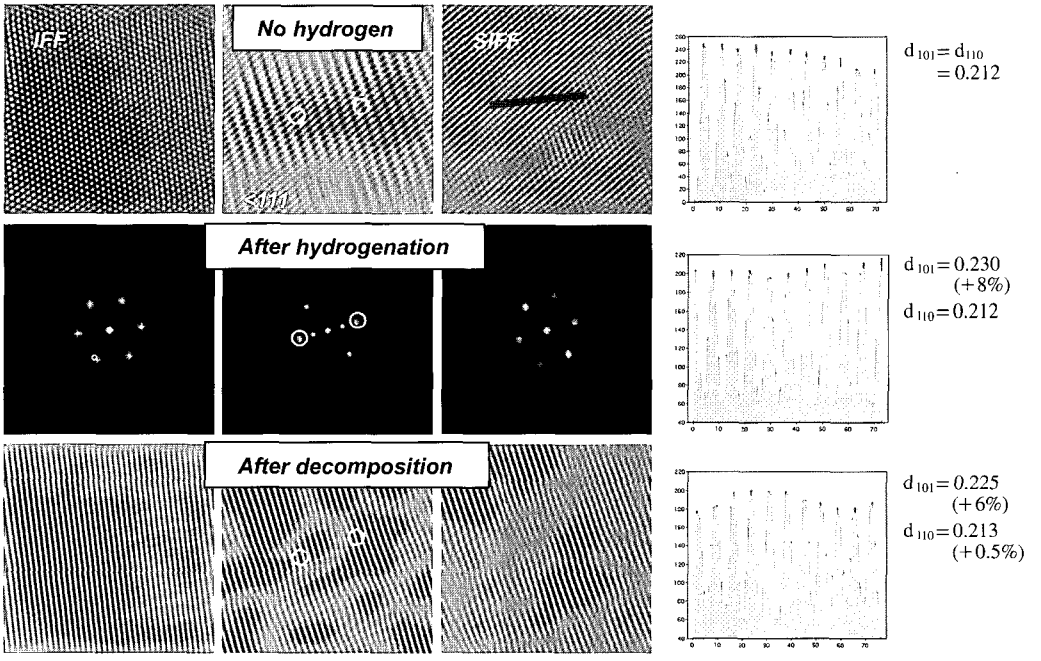

Fig. 7. Lattice image, local diffraction and selected lattice image from IFF, FFT and SIFFT. Mean lattice plane distance was estimated from SIFFT images.

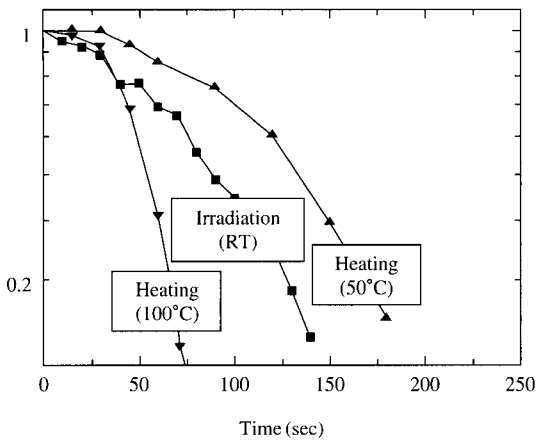

Fig. 8. Relative intensity of V_2H as a function of observation time at different temperature.

IFFT of the typical lattice plane in hydride area annealed at 50°C. We confirmed reproducibility for this hydride decomposition at the temperature range. The diffraction pattern from FFT shows the transition of bcc-bct-bcc, where the zone axis is $<111>$. A pair of {110} diffraction spots were selected for estimating plane distance. In the uncharged V sample, the plane distance of three pair of {110} was 0.212 nm, which means it is isotropic structure. In the H-charged specimen, the plane distance of (101) was 0.230 nm, but other sets of planes did not change, which means the hydride produced expanding unisotropic to [101] direction with +8%. After decomposition, FFT spots basically returned to bcc structure, but we observed some defective parts, and the plane distance of (101) was 0.225 nm, and the distance of (110) was 0.213 nm. It should be noted that V matrix remains the strain of +5% after H decomposition, which means that bcc lattice strained in solid solution at this temperature. It can be suggested some kind of H-trapping should be existed in solution condition.

Fig. 8 shows the changing of hydride fraction as a function of observation time. Beta hydride can be decomposed by heating within several minutes. In the case of intensive electron beam, the decomposition was enhanced, so it is a radiation-enhanced process.

CONCLUSIONS

The thermal stability of hydride in Vanadium has been studied by means of high resolution electron microscopy and in-situ heating experiment. Hydride (V_2H) is relatively stable at room temperature in vacuum condition. Hydride is decomposed during heating up to 100°C. In the structure of V_2H, hydrogen locates periodically at octa-headral sites, and shows bct structure with extending c-axis. Crystal orientation is basically $<110>$beta//$<110>$mat. Interface between hydride and matrix is in-coherent with large lattice strain of over 10%. Even after hydride decomposition, lattice expansion remains; this is due to dissolved hydrogen. Intensive electron beam enhances the decomposition, which means an irradiation-enhanced process.

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