Thermal Desorption of Hydrogen at the Titanium Hydride-Oxide Interface

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Changes in hydrogen distribution in δ -phase titanium hydrides ($\text{TiH}_{1.92\sim 1.95}$), covered with titanium oxide layers (TiO and TiO_2), were investigated by elastic recoil detection analysis (ERDA) after isochronal and isothermal annealing experiments. The hydrogen concentration near to the surface of the hydride exponentially decreased as a function of annealing time in the temperature range from 423 to 523 K. The result shows that the thermal desorption of hydrogen from the hydride is governed by first-order reaction kinetics and greatly depends on the thermal detrapping process. The thermal detrapping rates of hydrogen at the hydride-oxide interface were estimated and their activation energy was determined to be $1.3 \pm 0.2 \text{ eV}$.

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1. Introduction

The development of a hydrogen-air fuel cell consisting of proton-conducting oxides that act as a solid electrolyte and of hydrogen storage metals as a hydrogen source has been proposed by many workers.^{1,2)} This closed-type fuel cell, which does not require hydrogen gas to be supplied from outside, is promising as a compact electric power-generating system that would help to satisfy the growing demand for zero CO_2 -emitting energy sources. The rate of hydrogen transport to the fuel cell is one of the most important rate-determinant processes in the closed-type fuel cell. It is extremely important to understand how hydrogen is transported from the hydrogen storage metals to the proton-conducting oxides. Several reports have recently been published on the hydrogen diffusion, hydride dissociation and hydrogen evolution characteristics of titanium hydrides.^{3,4)} However, the surface of the hydride specimens is clearly oxidized, and the correlation between hydrogen migration and the oxide layers is as yet not fully understood.

In the present study, depth profiles of hydrogen atoms in the surface of titanium hydrides after annealing have been measured using an elastic recoil detection analysis (ERDA) which is a form of non-destructive ion beam analysis method with various energies that is used to investigate the thermal behavior of hydrogen atoms at the interface between the hydride and the oxide layers and the fundamental phenomenon leading to emission of atoms from the solid.

2. Experiments

Nonstoichiometric titanium hydrides were fabricated by maintaining the equivalent conditions for 4 days at a hydrogen pressure of $1.0 \times 10^5 \text{ Pa}$ and a temperature of 1073 K using a Sieverts apparatus. The H/Ti ratios of the hydride specimens were determined to be 1.92~1.95 by mass gain, hydrogen pressure changes as well as hydrogen analysis, was analyzed by means of high-energy ERDA using 2.8 MeV He^{2+} ions.⁵⁾ The hydride specimens were irradiated with He^{2+} ions at an incident angle of 75° to the surface normal of the specimen at room temperature. The hydrogen atoms forward-recoiled by elastic collisions were detected at a scattering angle of 30° to the incident ion direction. An

absorber comprising 12 μm -thick Al film was installed in front of the ERDA detector. In addition, a Rutherford backscattering spectrometry (RBS) measurement was simultaneously performed to act as an ion fluence monitor, in which the backscattered He^+ ions were detected at an angle of 170° to the incident ion direction. It was confirmed by X-ray diffraction (XRD) measurement that the hydride had a face-centered cubic structure (δ -phase) at room temperature. It was also observed by X-ray photoelectron spectroscopy (XPS) and co-axial impact collision ion scattering spectroscopy (CAICISS) measurements with Ar^+ ion sputtering at room temperature (Fig. 1(a)) and isochronal annealing for 10 min at several temperatures up to 551 K (Fig. 1(b)) that TiO and TiO_2 layers of about 10 nm thick were formed as the topmost surface on the hydride and were stable in this temperature region. The presence of hydrogen in the hydride phase has a considerable influence on oxidation dynamics, and the oxidation process takes place only on the hydride surface.⁶⁾ Moreover, a small amount of water, absorbed on the topmost surface, was observed by direct collision with the impinging primary ions, based on topmost surface-sensitive techniques consisting of CAICISS and low-energy ERDA using 2.0 keV He^+ ions.⁷⁾ The hydride specimens were irradiated with the pulsed He^+ ions at an angle of 0° to the surface normal of the specimens. The backscattered He^+ ions were detected at an angle of 180° to the incident ion direction by time of flight (TOF) using a co-axial micro channel plate (MCP) detector. In the low-energy ERDA measurement case, the hydride specimens were irradiated with the pulsed He^+ ions at an angle of 79° to the surface normal of the specimens. The hydrogen atoms that forward-recoiled at a scattering angle of 34° to the incident ion direction were detected by TOF with an MCP detector for ERDA. A small quantity of water remained on the topmost oxide layers after heating at 573 K for 10 min.

To investigate the thermal behavior of hydrogen at the hydride-oxide interface and hydride bulk, the hydrogen concentration in the hydride was measured by high-energy ERDA after isochronal annealing for 10 min at several temperatures to 573 K, and isothermal annealing in the temperature range from 423 to 523 K were carried out. The temperature of the specimens was measured with an alumel-chromel thermocouple in contact with the surface.

Fig. 1 XPS spectra of Ti 2p after (a) Ar^+ ion sputtering at room temperature and (b) isochronal annealing for 10 min at several temperatures up to 551 K.

Fig. 2 High-energy ERDA spectra of H recoiled from $\text{TiH}_{1.92}$ (●) before and after isochronal annealing for 10 min at (△) 473 K, (◆) 488 K and (▽) 498 K.

3. Results and Discussion

Figure 2 shows typical ERDA spectra of H recoiled from $\text{TiH}_{1.92}$ after annealing at each temperature for 10 min, measured using 2.8 MeV He^{2+} ion probe beams. The horizontal axis corresponds to several energies of the recoiled hydrogen atoms and represents the distance from the surface. The total integral counts of the ERDA spectra are almost the same until 398 K, but rapidly fall from 473 K. To obtain the depth profile, the averaged H counts to 10 channels in the ERDA spectra, the He^+ ion fluence, the elastic recoil cross-

Fig. 3 Hydrogen distributions in the surface of $\text{TiH}_{1.92}$ before and after isochronal annealing for 10 min at 398 K, 423 K, 473 K, 488 K, 498 K and 513 K.

sections of He^+ ion for H, the stopping cross-sections for H^+ and He^+ ions in TiH_x and the solid angle of the detection used were taken into account. The He^+ ion fluence, calculated from standard analysis of the RBS spectrum, was constant for all ERDA measurements. The stopping cross-sections change little, even if the hydrogen concentration decreases, because the stopping powers of H for H^+ and He^+ ions are much smaller than those of Ti for H^+ and He^+ ions. Although the elastic recoil cross-section varies according to the change in incident He^+ ion energy against the depth, the values are almost the same for all ERDA spectra that have been obtained after heating at several temperatures. Therefore, in the present study, the distribution of H, retained to around 300 nm deep in $\text{TiH}_{1.92}$, was estimated by normalizing the ERDA spectra from several temperatures to that at room temperature and then plotted in Fig. 3. It is of particular interest that the hydrogen concentration close to the surface changed to a much greater extent at 423~513 K than in the bulk. The hydrogen concentration to about 50 nm deep increased at 423 K but decreased at 473 K. The amount of H retained in the bulk at 488 K was higher than that in the surface. The depth profiles clearly show hydrogen migration. The hydrogen concentration gradient shows that hydrogen atoms, detrapped from the tetrahedral trap sites, are released with diffusion to the surface and hydrogen molecular recombination on the topmost surface. On the other hand, at 513 K, the hydrogen concentration near to the surface less than 50 nm in depth exceeded that in the bulk. It was found by low-energy ERDA combined with CAICISS that the increased presence of hydrogen at the surface can be ascribed to absorption of water on the uppermost oxide layers.

To identify the mechanism of the thermal re-mission of hydrogen from δ -phase $\text{TiH}_{1.95}$, isothermal annealing experiments were performed at 423, 473, 488, 493 and 523 K. The isothermal re-emission curves below 100 nm in depth at these temperatures are summarized as a function of annealing time in Fig. 4, where the vertical axis represents the retained number normalized by the number of H in $\text{TiH}_{1.95}$ before each annealing. The hydrogen concentrations at several temperatures decrease with increasing annealing time, and their decay rates increase as the annealing temperature

Fig. 4 Changes in hydrogen concentration near the surface below 100 nm in depth of $\text{TiH}_{1.95}$ as a function of annealing time at 423 to 523 K.

increases. The entire isothermal annealing curves can be approximated by one exponential function, as shown by the solid lines, since the vertical axis in Fig. 4 is scaled logarithmically. This result indicates that the thermal desorption of hydrogen from $\text{TiH}_{1.95}$ can be described by first-order reaction kinetics and greatly depends on the thermal detrapping process, since hydrogen release takes place through molecular recombination on the topmost surface after thermal detrapping of hydrogen from the trap sites followed by diffusion to the surface. Thus, the decay rate of the hydrogen concentration corresponds to the thermal detrapping rate. The thermal detrapping rates at several temperatures were determined from the slope of the solid lines in Fig. 4 and are plotted in kelvin as a function of $1000/T$ in Fig. 5. As a result, the activation energy of the thermal detrapping rate was determined to be 1.3 ± 0.2 eV from the slope of the solid line in Fig. 5. The activation energy is greater than that of 0.55 eV for the previously reported diffusion rate.³⁾ Therefore, the activation energy may correspond to the potential that is associated with intense lattice distortion at the interface between the hydride and oxide layers.

The oxide layers play an important role as surface barriers for hydrogen retention in hydrogen storage metals, since they impede hydrogen transport. Since the hydrogen desorption from the hydrides is controlled by the oxide layers, it will be

Fig. 5 Arrhenius plots of thermal detrapping rates of hydrogen in $\text{TiH}_{1.95}$ at 423 to 523 K.

necessary to use various techniques to modify the hydride-oxide interface to further enhance hydrogen transport from the hydrogen storage metals to the proton-conducting oxides and enable the process to take place at a lower temperature.

4. Summary

The δ -phase $\text{TiH}_{1.92\sim 1.95}$ specimens were prepared by adjusting the gas pressure and the temperature by means of a Sieverts apparatus. It was confirmed by XPS and CAICISS, combined with low-energy ERDA, that the hydrides were covered with titanium oxide layers about 10 nm thick, and, moreover, a small quantity of water was dissociated on the oxide topmost surface. After isochronal annealing at several temperatures to 573 K for 10 min, the changes in the hydrogen distribution near to the surface (to about 300 nm deep) of the hydride were investigated using high-energy ERDA. The re-emission of hydrogen from the hydride started at 473 K. Hydrogen migration and release were clearly shown in the depth profiles.

To clarify the thermal behavior of hydrogen from the hydride to the oxide layers, isothermal annealing experiments were carried out in the temperature range of 423 to 523 K. The isothermal re-emission curves at each temperature were approximated by one exponential function. This fact suggests that the thermal re-emission of hydrogen from titanium hydride is governed by first-order reaction kinetics. Notably, the thermal detrapping of hydrogen from the trap sites plays the most important role in the thermal release. The thermal detrapping rates were estimated and their activation energy was determined to be 1.3 ± 0.2 eV, which was greater than that of 0.55 eV for the diffusion rate, from analysis of the re-emission curves. Therefore, the activation energy may correspond to the potential energy at the surface barrier, and the hydrogen migration rate may depend primarily on the characteristics of the hydride-oxide interface.

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