

Measurement of the transport of hydrogen isotopes near the surface of metal-hydride and deuteride using elastic recoil detection technique

B. Tsuchiya *, S. Nagata, K. Toh, T. Shikama

Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

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Abstract

The thermal behavior of hydrogen isotopes near the surface of δ -phase titanium hydride and deuteride covered with an oxide layer has been investigated using the elastic recoil detection (ERD) technique. The hydrogen isotopes concentrations near to the surface of the hydride and deuteride decreased exponentially as a function of annealing time in the temperature range of 423–488 K. Also a hydrogen concentration gradient is formed at the surface. The change of the hydrogen distribution with annealing time at several temperatures was analyzed using mass balance equations in which elementary processes such as diffusion, trapping and detrapping at vacant trap sites are taken into account. The effective diffusion rates of hydrogen isotopes to the topmost oxide layer and thermal detrapping rates of hydrogen isotopes at the hydride–oxide interface were estimated. Moreover, the activation energies for the effective diffusion rate and the thermal detrapping rate were determined to be 0.54 ± 0.10 and 1.20 ± 0.02 eV, respectively.

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1. Introduction

Titanium hydride and deuteride have potential for use as hydrogen sources in hydrogen-air fuel cells including proton-conducting oxides that act as solid electrolytes [1,2]. The rate of hydrogen transport at the interface between hydrides and oxides is one of the most important rate-determining processes in the fuel cell. However, the correlation between hydrogen migration and the oxide layers is as yet not fully understood.

In the present study, measurements of transport of hydrogen isotopes near the surface of hydride and deuteride, covered with titanium oxide, have been carried out using elastic recoil detection (ERD) technique with

2.8 MeV He^{2+} ion beams [3], and the experimental data have been analyzed using mass balance equations [4] including fundamental phenomena leading to hydrogen migration to the surface.

2. Experiments

Titanium hydride ($\text{TiH}_{1.95}$) and deuteride ($\text{TiD}_{1.96}$) specimens were prepared using a Sieverts apparatus [3]. These specimens have a non-stoichiometric face-centered cubic structure (δ -phase). It was observed in X-ray photoelectron spectroscopy (XPS) and co-axial impact collision ion scattering spectroscopy (CAICISS) measurements that titanium oxide layers about 10 nm thick were formed on the topmost surface of the specimens. It was also observed by low-energy ERD technique using 2.0 keV He^+ ions and high-energy ERD technique using 2.8 MeV He^{2+} ions

* Corresponding author. Tel.: +81 22 215 2063; fax: +81 22 215 2061.
E-mail address: tsuchiya@imr.tohoku.ac.jp (B. Tsuchiya).

that a small quantity of water was adsorbed on the topmost oxide layer.

The concentrations of hydrogen isotopes, retained in the specimens after isothermal annealing at temperatures of 423–488 K by means of a tungsten–ceramics heater, were measured using high-energy ERD technique. The hydrogen isotopes, forward-recoiled by elastic collisions with the incident He^{2+} ions, were detected at a scattering angle of 30° to the incident ion direction. Simultaneously, the He^{2+} ion fluence was also measured by detecting the He^{2+} ions back-scattered at an angle of 170° to the incident ion direction. The temperature of the specimens was measured with an alumel–chromel thermocouple in contact with the surface.

3. Results and discussion

Fig. 1 shows typical ERD spectra of H recoiled from $\text{TiH}_{1.95}$ after annealing at 488 K for 15, 35 and 85 min, measured using 2.8 MeV He^{2+} ion probe beams. The number of counts due to H recoils in the ERD spectra decreases with increasing annealing time. Typical ERD spectra of D recoiled from $\text{TiD}_{1.96}$ were also measured, and a reduction of the number of counts due to D recoils was observed as the annealing time increased. To obtain the depth profiles of H and D, the H and D counts averaged over 10 channels in the ERD spectra, the He^+ ion fluence, the elastic recoil cross-sections of He^+ ion for H and D, the stopping cross-sections for H^+ , D^+ and He^+ ions in TiH_x and TiD_x , the solid angle of the detection used were taken into account. The He^+ ion fluence, calculated from a standard analysis of the RBS spectrum, was constant for all ERD measurements. The stopping cross-sections change little, even if the hydrogen concentration decreases, because the stopping powers of H (D) for H^+ (D^+) and He^+ ions are much smaller than those of Ti for H^+ (D^+) 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 ERD spectra that have been obtained after heating at several temperatures.

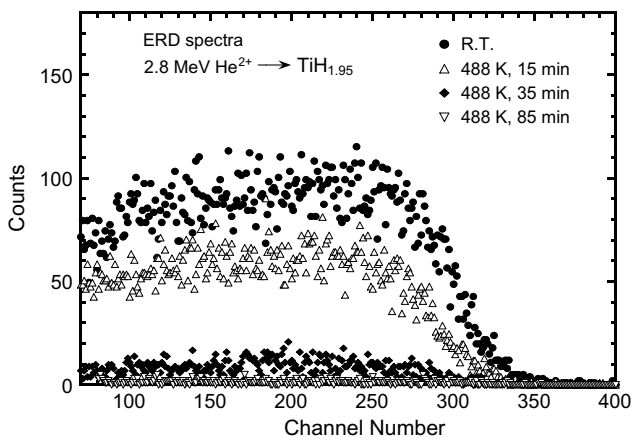


Fig. 1. ERD spectra of H recoiled from $\text{TiH}_{1.95}$ before and after isothermal annealing at 488 K for 15, 35 and 85 min.

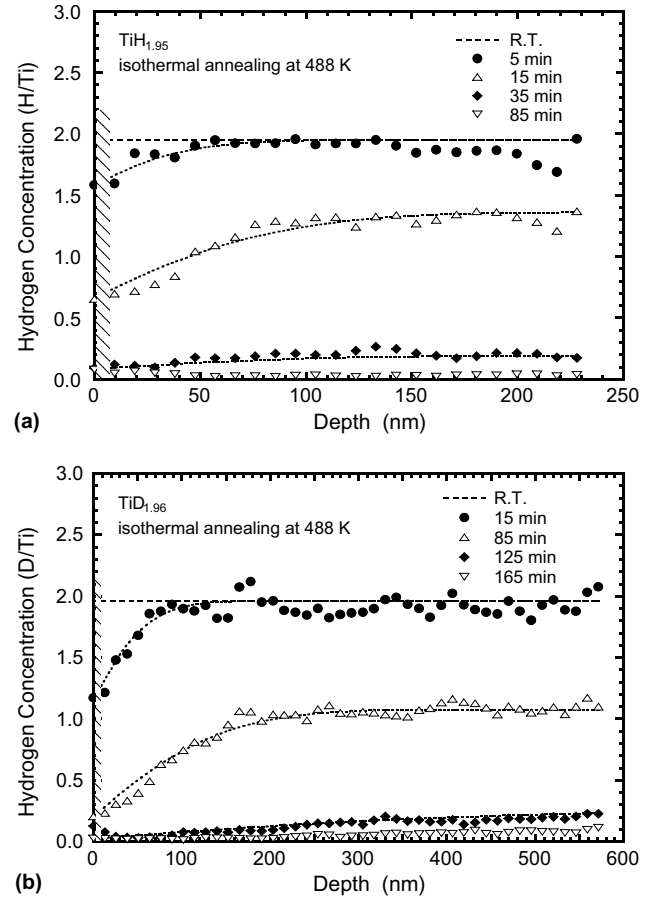


Fig. 2. Depth profiles of H and D near the surface of (a) $\text{TiH}_{1.95}$ and (b) $\text{TiD}_{1.96}$ before and after isothermal annealing at 488 K for several times.

Fig. 2(a) and (b) show depth profiles of H and D, determined in a depth range of around 230 nm in $\text{TiH}_{1.95}$ (around 570 nm in $\text{TiD}_{1.96}$), after isothermal annealing at 488 K for several times, respectively. In Fig. 2(a) and (b) the titanium oxide layers are indicated as striped areas. It is of particular interest that the hydrogen concentration close to the surface changed to a much greater extent than in the bulk. The depth profiles clearly show hydrogen migration. The concentrations of H and D below 100 nm deep decreased exponentially as a function of annealing time at several temperatures. It is assumed that the hydrogen migration from the bulk to the surface takes place by diffusion with trapping and detrapping at vacant trap sites, and finally the hydrogen atoms are emitted by molecular recombination on the topmost oxide layer after jumping the hydride–oxide interface.

Based on these assumptions, the depth profile of retained hydrogen can be simply expressed using mass balance equations as follows [4]:

$$\frac{dn^i(x, t)}{dt} = D^i \frac{\partial^2 n^i(x, t)}{\partial x^2} + \sum_d n_T^i(x, t) - \sum_T^i (C_0 - n_T^i(x, t)) n^i(x, t), \quad (1)$$

$$\frac{dn_T^i(x, t)}{dt} = -\sum_d n_T^i(x, t) + \sum_T^i (C_0 - n_T^i(x, t)) n^i(x, t), \quad (2)$$

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