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Journal of Nuclear Materials 258–263 (1998) 622–627

journal of nuclear materials

Deuterium migration in titanium during deuteron irradiation observed by proton spectra of the d(d,p)t reaction

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Abstract

From analysis of proton spectra associated with the d(d,p)t reaction, deuterium depth profiles in titanium during 130-keV deuteron irradiation at temperatures from 260 to 360 K were obtained as a function of the irradiation time. This nuclear reaction analysis technique (NRA) was applicable to in situ depth profiling in the region from the surface to the depth of 0.6 μm in titanium. The depth resolution varied depending on the depth; 0.07 μm at the surface and 0.15 μm at the depth between 0.2 μm and 0.6 μm. The observed depth profiles gave a clue to the dynamics of deuterium migration in titanium.

1. Introduction

To develop fusion reactor materials, a number of studies have been carried out on migration or diffusion, trapping, sputtering, reemission and thermal release of isotopic hydrogen species in plasma facing materials as well as tritium breeding blanket materials. For blanket materials, research subjects have been focused on the tritium diffusion in and thermal release from neutron-irradiated lithium-containing materials such as Li_2O, $LiAlO_2$, Li_2SiO_3 and Li_2TiO_3, and the tritium diffusion data required for designing blanket systems of fusion reactors have been accumulated by measuring thermal release rates [1–5]. For plasma facing materials, on the other hand, much attention has been paid to the chemical and physical sputtering induced by interactions with energetic isotopic hydrogen ions because the sputtered species would affect the condition of plasmas in fusion reactors. Until now a great deal of knowledge has been accumulated on the sputtering of isotopic hydrogen species for such materials as graphite, SiC, B_4C and low-Z metals.

However, much remains to be solved for understanding a mechanism of hydrogen migration in plasma facing materials. Although there are many theoretical models or simulations on the dynamics of hydrogen migration in plasma facing materials with emphasis on graphites [6–9], experimental data available for verifying models are limited due to experimental difficulties. The use of the d(d,p)t reaction [10,11] would be one of the possible means of in situ observation of hydrogen migration, because the nuclear reaction should directly reflect the concentration gradient or depth profile of deuterium incorporated into materials. From early 1970s the nuclear reaction analysis (NRA) using the d(d,p)t and $d(^3He,p)^4He$ reactions has been applied to deuterium depth profiling in fusion materials like Ti and TiC [12–14].

In the present work, we have developed a new procedure for numerical analysis of proton spectra associated with the d(d,p)t reaction to observe deuterium migration in materials during deuteron irradiation. The analysis provides deuterium depth profiles from the surface to the depth of 0.6 μm in titanium irradiated with 130-keV deuterons, and gives a clue to the dynamics of deuterium migration in titanium.

2. Experimental

The surface of titanium plates (0.2 mm in thickness, 99.5% of purity) from NIRACO was polished with emery paper and washed with acetone in a supersonic bath. The sample materials were irradiated in a vacuum with 130-keV deuterons from a Cockcroft–Walton accelerator of our laboratory. The samples were attached on a

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0022-3115/98/$19.00
PII: S0022-3115(98)00244-X

sample holder in a scattering chamber (Fig. 1). The temperature of the samples, controlled by a combination of cooling with liquid nitrogen and heating with a ceramic heater, was measured with a thermocouple welded to the sample. The deuteron beam was collimated to a circular spot of 2.8 mm in diameter at the surface of the sample. The beam current, measured with a Faraday cup, was in the range from 1 to 3 μA or $(1-3)\times 10^{14}$ D^+ cm^{-2} s^{-1}.

To detect protons emitted from the sample as a result of the d(d,p)t reaction, a silicon surface barrier detector (SSD, 150 μm in thickness and 150 mm^2 in area) was placed at 144° toward the beam direction. In front of the detector, an aluminum absorber (6 μm thick) and a set of slits were placed to assure the accuracy of detection without exposure to scattered particles. The counting efficiency of the detector was calibrated with standard α emitters.

3. Analysis of proton spectra

When the kinetic energy of incident deuterons, E_d, is constant, the energy of protons, E_p, is expressed in general as

$$E_p = \left[\Psi + \sqrt{\Psi^2 + \frac{m_t}{m_t + m_p}\left\{Q + E_d\left(1 - \frac{m_d}{m_t}\right)\right\}}\right]^2, \quad (1)$$

with

$$\Psi = \frac{\sqrt{m_d m_p E_d}}{m_t + m_p}\cos\,\theta_{lab},$$

where m_p, m_d and m_t are the masses of proton, deuteron and triton, respectively; Q is the Q value of the d(d,p)t reaction and θ_{lab} the scattering angle of proton in the laboratory system. The angular distribution $W(\theta)$ is given by the following equation with $a_2 = 0.44 \pm 0.03$, $a_4 = 0.04 \pm 0.03$, $Q_2 = 0.999$ and $Q_4 = 0.996$ reported by Krauss et al. [10]:

$$W(\theta) = 1 + a_2 Q_2 P_2(\theta) + a_4 Q_4 P_4(\theta), \quad (2)$$

where a_i is the angular distribution coefficient, Q_i the attenuation coefficient, and $P_i(\theta)$ the Legendre Polynominals ($i = 2,4$).

The excitation function, $\sigma(E_d)$, for the d(d,p)t reaction in the energy range 6–240 keV is given by the equation [10]

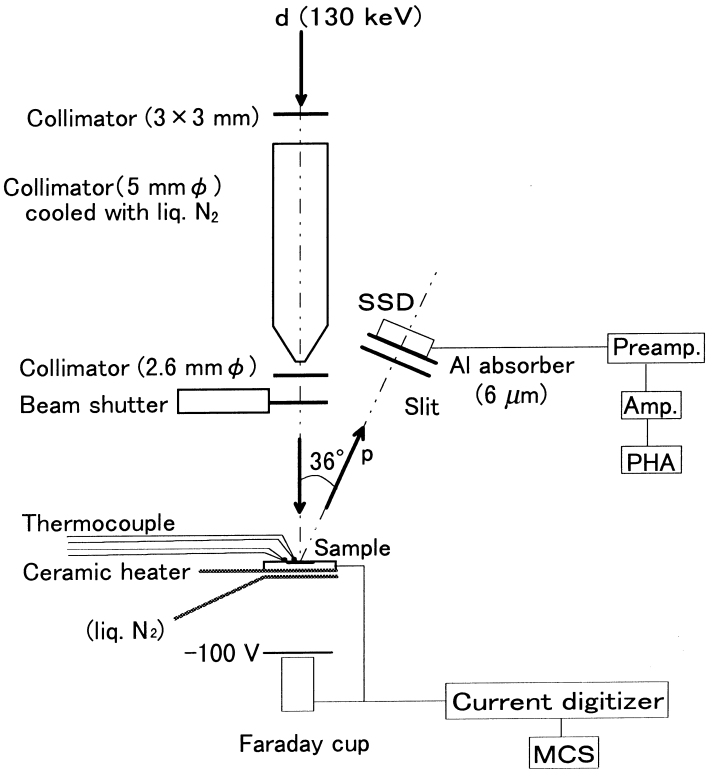

Fig. 1. Experimental setup in scattering chamber used for measuring proton spectra.

$$\sigma(E_d) = \left(\frac{105.8}{E_d} + 0.019 + 0.00096E_d\right) \times \exp\left(-\frac{e^2}{\hbar}\sqrt{\frac{m_d}{2E_d}}\right). \quad (3)$$

When a solid is irradiated, the incident deuteron loses its kinetic energy in the course of penetration in target materials. It is possible to estimate the deuterium energy at any depth of penetration by calculations with the TRIM95 code [15], and the excitation function can be rewritten in the form $\sigma(x)$ that represents the cross section as a function of the depth.

Because the counting rate of protons emitted with a certain energy is proportional to the number of incident deuterons per second, N_d, the deuterium concentration, $C(x)$, at a depth, x, and the cross section, $\sigma(x)$, for the d(d,p)t reaction, we can derive the following equation which connects the counting rate of protons, I_p, at a fixed energy (or channel in practical detection) and the deuterium concentration, $C(x)$,

$$I_p = C(x) \times N_d \times \sigma(x) \times \Delta(x) \times \Omega \times \frac{W(\theta')}{4\pi \int_0^{\frac{\pi}{2}} W(\theta) \sin\theta \, d\theta}, \quad (4)$$

where Δx is the width in depth corresponding to an channel width in the proton spectra to be measured, Ω the solid angle of a detector and θ' the position angle of a detector in the center-of-mass system.

Here, both I_p and N_d are known directly from measurements, $\sigma(x)$ is converted from $\sigma(E_d)$ using stopping power calculated by the TRIM program, and we can obtain the deuterium concentration, $C(x)$, as a function of the depth. When titanium is irradiated with 130-keV deuterons, as in the present work, the energy of the emitted protons is distributed in the energy range between 2.5 and 2.8 MeV. The relation between the proton energy, E_p, and the depth, x, obtained in the present calculation is shown in Fig. 2.

Fig. 3 shows proton spectra calculated for various depths in titanium irradiated with 130-keV deuterons. For the calculation, the deuterium concentration was assumed to be uniform in the target. The shape of proton spectra varies depending on the depth. The energy of protons emitted from a larger depth is higher than that from a smaller depth, and the peak position tends to shift toward a lower-energy side with a decrease of the depth. In contrast, the counting rate for protons emitted from a larger depth is lower than that from a smaller depth. The full width at half maximum (FWHM) of the proton spectra also varies depending on the depth. From these features of proton spectra, we can evaluate the depth resolution and the detection limit or sensitivity as shown in Fig. 4. The depth resolution is 0.07 μm at the surface and about 0.15 μm at the depth between 0.2 μm and 0.6 μm. The detection limit is approximately 5×10^{19} cm^{-3} from the surface to the depth of 0.4 μm, but it increases abruptly in the region deeper than 0.5 μm. These values are comparable with those of other techniques like NRA with the d(^{3}He,p)^{4}He reaction [12,13] and the elastic recoil detection (ERD) with high energy ^{4}He [16]. The present technique is applicable to the deuterium depth profiling for the depth between the front surface and 0.6 μm in titanium irradiated with 130-keV deuterons. A computer program for numerical calculations of depth profiling developed here is reported elsewhere [17].

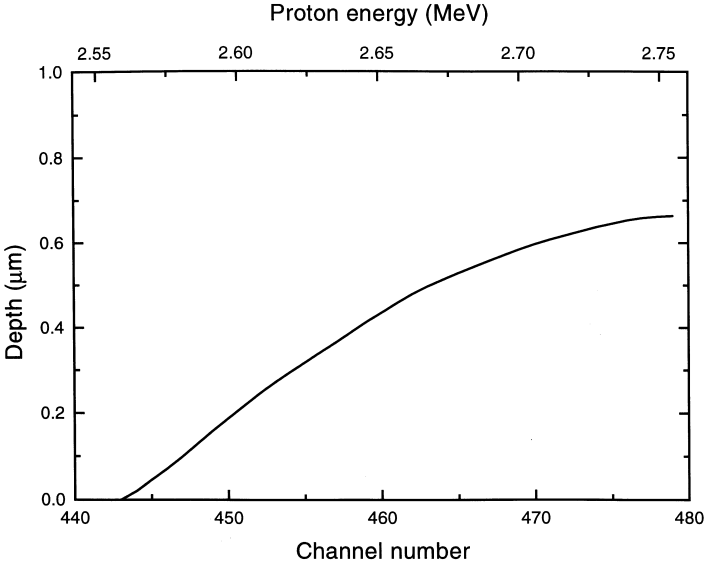

Fig. 2. Relation between the energy of proton from the d(d,p)t reaction and the depth x in titanium irradiated with 130-keV deuterons.

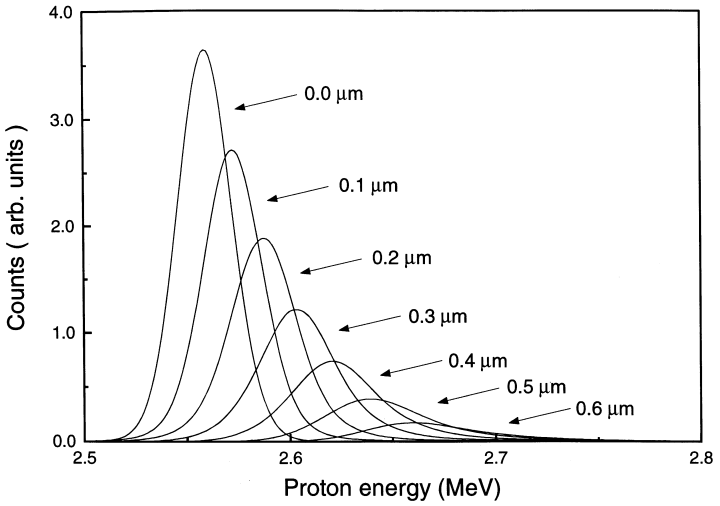

Fig. 3. Energy spectra of protons emitted from various depths in titanium irradiated with 130-keV deuterons; calculated by assuming a uniform deuterium concentration in titanium.

4. Results and discussion

From analysis of the proton spectra, we have obtained deuterium depth profiles in titanium irradiated at 260 K up to 100 ks at the deuteron flux of 2.5×10^{14} D^+ cm^{-2} s^{-1} as shown in Fig. 5, where the depth profiles are illustrated 10 ks apart. Although the mean range of 130-keV deuterons in titanium is estimated to be 0.90 μm from the TRIM code, the deuterium depth profile was drawn with satisfaction only for the region from the surface to the depth of 0.6 μm, because in the region deeper than 0.6 μm the sensitivity was insufficient arising mainly from a lower probability of the d(d,p)t reaction.

As seen in Fig. 5, the deuterium depth profile was obtained when the titanium was irradiated for more than 10 ks or to the fluence more than 2.5×10^{18} D^+ cm^{-2}. The profile was broad at the depth from 0.4 to 0.6 μm and its deuterium concentration was around 1.7×10^{22} cm^{-3}. Here, most of deuterium would be trapped in the region deeper than 0.6 μm. The deuterium concentration at the surface was 0.4×10^{22} cm^{-3}. As the irradiation is continued, the total amounts as well as the deuterium concentration at the surface increased. Deuterium migrated toward the surface and was stored at the near surface region. The deuterium release rate or recombination coefficient should be fairly small at 260

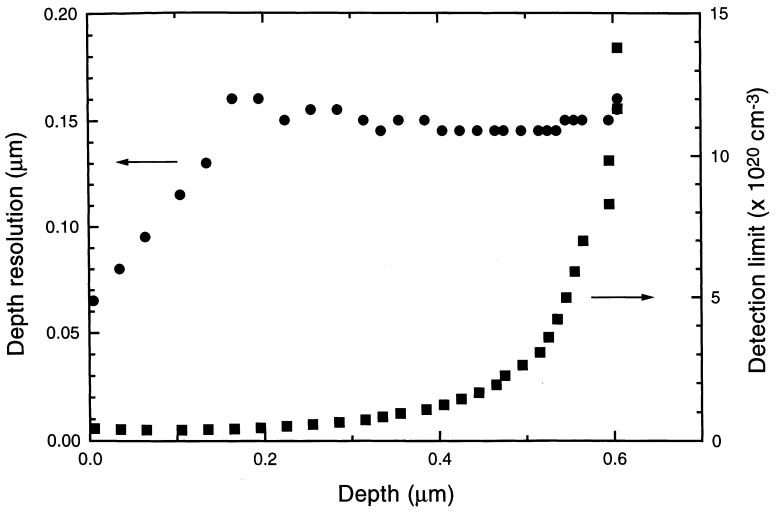

Fig. 4. Plots of depth resolutions and detection limits against the depth in titanium irradiated with 130-keV deuterons.

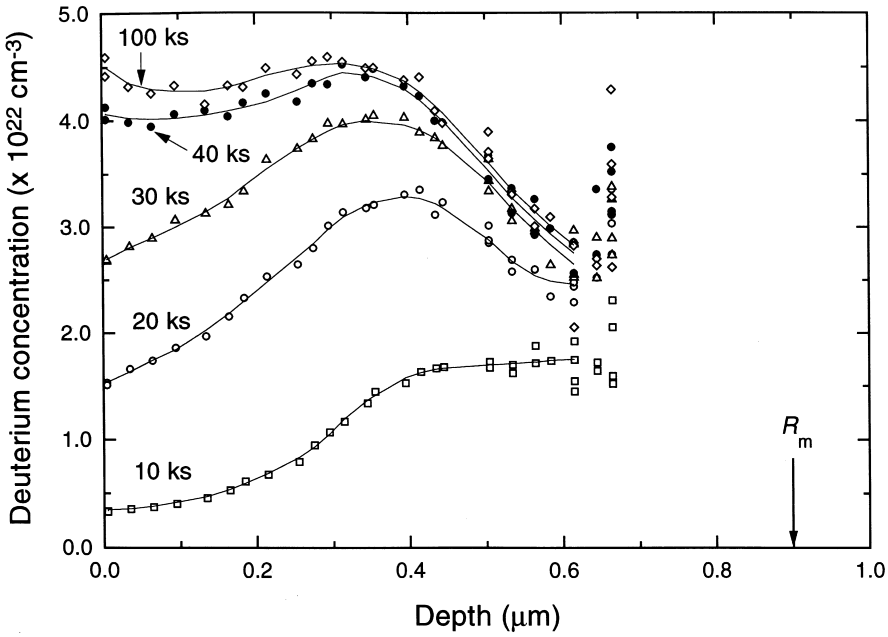

Fig. 5. Snapshots of deuterium depth profiles in titanium irradiated at 260 K. The deuteron fluences are 2.5×10^{18} D^+ cm^{-2} at 10 ks, 5.0×10^{18} D^+ cm^{-2} at 20 ks, 7.5×10^{18} D^+ cm^{-2} at 30 ks, 1.0×10^{19} D^+ cm^{-2} at 40 ks and 2.5×10^{19} D^+ cm^{-2} at 100 ks. R_m indicates the mean range (0.90 μm) of 130-keV deutrons in titanium. The deuterium concentrations in the depth larger than 0.6 μm were not determined because of experimental difficulties.

K. After 40 ks of irradiation (1.0×10^{19} D^+ cm^{-2}), deuterium was widely distributed from the surface to the depth of 0.5 μm with a broad peak around 0.3–0.4 μm. The difference in the deuterium concentrations between the peak region (4.5×10^{22} cm^{-3}) and the near surface region (4.0×10^{22} cm^{-3}) became small. When the titanium was irradiated for 100 ks (2.5×10^{19} D^+ cm^{-2}), a deuterium buildup appeared just inside the surface, although the total deuterium concentration was comparable with that for the 40-ks irradiation. Namely, the deuterium concentration was saturated at 4.5×10^{22} cm^{-3}, a balance (steady state) being attained between the incoming and outgoing deuterium fluxes.

The deuterium concentration at the steady state attained by irradiation to the fluence of 2.5×10^{19} D^+ cm^{-2} corresponds to approximately 0.8 of the D/Ti atomic ratio. The ratio is smaller than the value (1.6–2.0) reported for the stable titanium deuteride (TiD_2) formation at the fluences $\geqslant 10^{19}$ D^+ cm^{-2} [18]. The low D/Ti ratio observed here reveals that reemission of deuterium occurred even at 260 K during the deuteron irradiation.

Fig. 6 illustrates the depth profiles at the steady state attained by irradiation to the fluence of 1.0×10^{19} D^+ cm^{-2} at 320 and 360 K, together with that at 260 K. The total deuterium concentration both at 320 and 360 K is clearly lower than that at 260 K. The deuterium concentration at the surface was greatly reduced when the temperature was raised to 320 and 360 K. The result indicates that the thermal release rates of deuterium increase with increasing temperature. The deuterium concentration at the surface was 1.3×10^{22} cm^{-3} at 320 K and 1.0×10^{22} cm^{-3} at 360 K. The recombination coefficient at 360 K should be slightly higher than that at 320 K but much higher than that at 260 K. A broad peak is still seen around 0.3 μm in the depth profile at 320 K, while the profile is rather flat at 360 K. This difference in the shape of the depth profile would reflect the temperature dependence of diffusivity of deuterium in the bulk.

5. Summary

We have observed deuterium migration in titanium during irradiation with 130 keV deuterons at 260, 320 and 360 K by the deuteron depth profiling using NRA with the d(d,p)t reaction. In this work, the emphasis was laid on establishing an analytical procedure of the proton spectra. This NRA was applicable to in situ depth profiling in the region from the front surface to 0.6 μm in titanium. For the depths larger than 0.6 μm, the sensitivity was not sufficient to derive the depth profile because of the low sensitivity arising from the low cross section for the d(d,p)t reaction. The detection limit was $(0.5–1) \times 10^{20}$ D cm^{-3} in the region between the surface

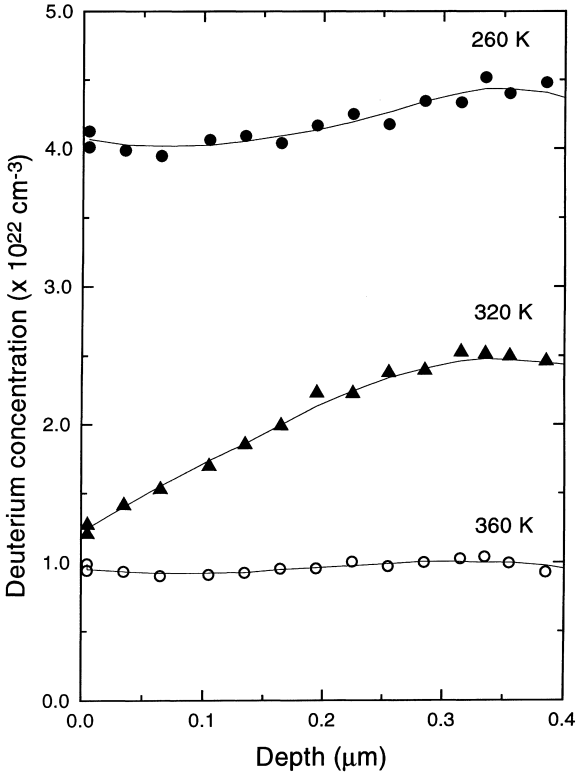

Fig. 6. Deuterium depth profiles in titanium irradiated for 40 ks to the fluence of 1.0×10^{19} D^+ cm^{-2} at 260, 320 and 360 K.

and 0.4 μm. The depth resolution was 0.07 μm at the surface and 0.15 μm for the depth larger than 0.2 μm. The simultaneous use of a single deuterium beam for both the implantation and detection in this NRA can be advantageous for investigation of dynamics of deuterium migration in materials during deuteron irradiation. We are continuing the work to accumulate more data necessary for discussing diffusion and recombination processes of deuterium in materials.

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