ELSEVIER

Journal of Nuclear Materials 248 (1997) 42–45

journal of nuclear materials

Retention of hydrogen isotopes in beryllium by simultaneous H^+ and D^+ irradiation

B. Tsuchiya *, K. Morita

Department of Crystalline Materials Science, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku Nagoya 464-01, Japan

Abstract

The concentration profiles of H and D retained in beryllium by simultaneous dual H^+ and D^+ ion irradiation at room temperature and on post isochronal annealing have been measured by means of the elastic recoil detection (ERD) and Rutherford backscattering (RBS) techniques. It has been found that as the irradiation time increases, the concentrations of H and D retained increase linearly in the beginning of the irradiation and hereafter that of H saturates faster than that of D. The ratio of the concentration of D to H at steady state was determined to be 1.2 ± 0.1. The isotope ratio is in good agreement with the theoretical one (1.25) calculated from the kinetic equations for free and trapped hydrogen species at steady state and local equilibrium, in which the diffusion-limited rate constants for the trapping, local molecular recombination and the ion-induced detrapping cross-section are taken into account. It has also been found from the isochronal annealing curve that there are two stages at 363 K and 573 ± 100 K and the re-emission rate of H is the same as that of D at the lower stage and is faster at the higher stage, which is so-called isotope effect. © 1997 Elsevier Science B.V.

1. Introduction

In magnetically confined fusion devices where low-Z materials such as carbon, boron and beryllium are used as plasma facing components, it has been demonstrated to produce fusion powers of 1–10 MW in D–T discharge experiments [1,2]. In order to achieve the ignition condition during long term D–T discharge, it is of essential importance to evaluate and predict the transient recycling fluxes of hydrogen isotopes from the plasma facing components. For this purpose, so far, the retention and re-emission processes of hydrogen isotopes in graphite have been extensively studied by many authors [3–8]. A little data on beryllium have been accumulated [9–11]. It has been shown by means of the nuclear reaction analysis (NRA) technique that there exist two stages in the isochronal re-emission curves of deuterium implanted into beryllium up to saturation [9]; a stage at 393 K and a broad stage around 573 K, which corresponds to retention only at the low ion fluence. However, the retention and re-emission processes are not well understood yet, because the beryllium surface is easily oxidized. In order to understand well the processes, it is necessary to separate the effect of oxidized layers from data on the bulk [12].

Very recently, the present authors have shown by means of the elastic recoil detection (ERD) technique that the isochronal re-emission curve has three stages, namely the broad stage consists of two stages from the oxidized surface layers and the projected range in the bulk [13]. It has been also shown by means of the thermal desorption technique that there exist three emission peaks in the desorption spectra [14]. From the analysis of the isothermal re-emission curves at temperatures from 323 to 673 K, the activation energies at three stages have been determined to be 0.14, 0.26 and 0.89 eV, respectively [13]. The lowest activation energy of 0.14 eV was ascribed to dissociation of linear chain clusters of Be-dihydride molecules and the ones of 0.26 and 0.89 eV were ascribed to thermal detrapping from traps in Be-oxide and defects such as void and bubble, respectively [13]. In order to understand these data in detail, further systematic studies are necessary.

In this paper, we report the experimental data on retention of H and D in beryllium by independent and simultaneous irradiation of H^+ and D^+ ions and on post isochronal

---

* Corresponding author. Fax: +81-52 789 3791; e-mail: k.morita@mail.nucl.nagoya-u.ac.jp.

0022-3115/97/$17.00
PII S0022-3115(97)00149-9

annealing. The isotope ratios of the concentrations of D to H retained at steady state are found to be 1.2 ± 0.1 on both irradiation, which is so-called isotope effect. The re-emission curve by isochronal annealing of hydrogen retained by simultaneous H^+ and D^+ irradiation shows that there exists no isotope difference at the lower temperature stage, but at the higher temperature stage.

2. Experiments

Beryllium specimens used were disc plates of 30 mm in diameter and 1 mm in thickness and with a mirror-likely flat surface (99 at.% in purity from Bruch-Wellman Co.) which were in a commercial grade. The RBS measurement showed that there were impurities of 0.93 at.% oxygen and little heavier in the bulk and oxidized surface layers of about 7 nm in thickness. The specimen was placed on a manipulator in contact with a ceramic heater in a UHV chamber which was usually evacuated to the base pressure less than 1×10^{-7} Pa. The residual hydrogen atoms in the specimen were removed out by heating it at 923 K for 20 min. The oxidized surface layers were always removed out by sputtering with 0.5 keV Ar^+ ions at a angle of 60° to the surface normal so that the RBS intensity of oxygen surface peak was not detected.

The specimen was independently or simultaneously irradiated up to saturation (2.2×10^{22} H + D ions/m^2) at room temperature with 4 keV H_2^+ and 3 keV D_2^+ ions at the angles of 20° and 35° to the surface normal, respectively [15], so that the peak depths of the depth distributions correspond with each other. Both of the ion beams were independently generated from two differentially pumped ion guns of a commercial type, into which the working gases of H_2 and D_2 were introduced to a constant pressure of 4×10^{-2} Pa through a liquid-nitrogen cold trap. Then the pressure of main chamber was kept below 5×10^{-5} Pa during ion gun operation. The fluxes of H^+ and D^+ ion beams were independently selected to be 4.3×10^{17} ions/$m^2 \cdot s$, respectively. After the irradiating up to saturation, isochronal annealing of the specimen was done for 10 min at several temperatures from 323 to 723 K. Since the ion guns were not equipped with the mass analyzer, oxidized layers of 7 nm were produced by the H^+ and D^+ ion implantation. The thickness of oxidized layers was not changed by isochronal annealing.

The concentrations of H and D retained in the specimen were measured at room temperature by means of the ERD technique with He^+ ion probe beam of 1.7 MeV. The fluence was simultaneously monitored by means of the RBS technique. The analysis beam fluence used did not affect the retention concentrations of H and D in the specimen. Since a number of small voids, bubbles and blisters were found in the irradiated region of the specimen by the SEM observation after the thermal annealing, a set of irradiation and thermal annealing was always done for non-irradiated part of the specimen.

3. Experimental results

3.1. Retention

The specimens of beryllium were simultaneously irradiated with dual ion beams of 3 keV D_2^+ and 4 keV H_2^+ ions up to saturation and the concentrations of H and D retained were measured at several stages of the implantation by means of the ERD technique. The concentrations (hydrogen/Be) estimated from the counts averaged over 40 channels around the H and D peaks in ERD spectra are plotted as a function of irradiation time in Fig. 1. The concentrations of H and D to Be are calculated using the He^+ ion fluence, the solid angle of the detector, the recoil cross-sections of He^+ ion for H and D [16] and the stopping cross-sections for H^+, D^+ and He^+ ions by the standard analysis technique. The contribution of tailing of the D peak to the H peak was subtracted using the ERD spectra obtained with independent D^+ ion irradiation under the same experimental condition, of which the peak height is same as that for dual ion irradiation. It is seen from Fig. 1 that both concentrations of H and D increase rapidly in the beginning of the time and hereafter that of H saturates faster than that of D. Then the concentration ratio of D to H, n_T^D/n_T^H, at steady state can be determined to be 1.2 ± 0.1, which is so-called isotope effect for the retention of hydrogen isotopes in beryllium. The error in the D/H ratio is mainly ascribed to uncertainty in the recoil cross-sections.

For comparison, the concentrations of H and D retained by independent irradiations with 4 keV H_2^+ or 3 keV D_2^+ [13] are also shown in Fig. 1. It is seen from Fig. 1 that the retention behaviors of H and D on the independent implan-

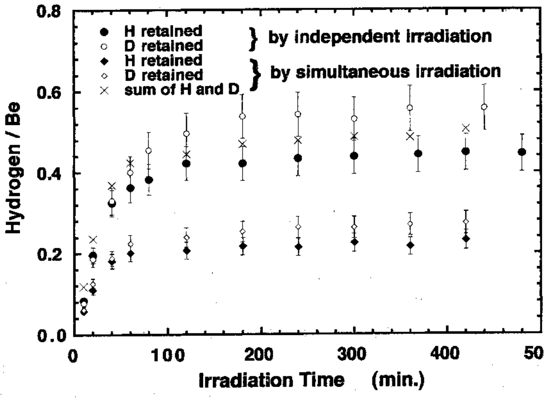

Fig. 1. Transient curves of the concentrations of H and D (hydrogen/Be) retained in beryllium by independent and simultaneous irradiation of 4 keV H_2^+ and 3 keV D_2^+ at room temperature.

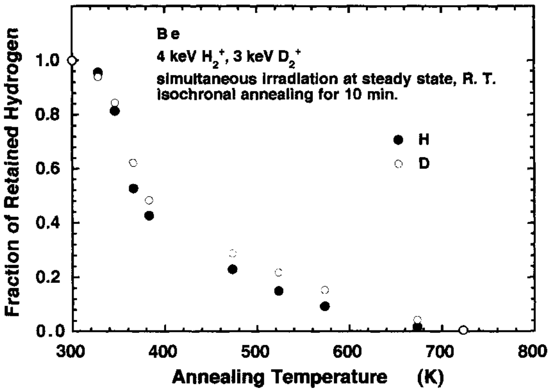

Fig. 2. Isochronal annealing curves of H and D in beryllium implanted by simultaneous irradiation of 4 keV H_2^+ and 3 keV D_2^+ up to saturation at room temperature. The heating time was 10 min.

tation are very similar to those on the simultaneous implantation and the value of n_T^D/n_T^H at steady state on the independent implantation is also accidentally the same as that on the simultaneous implantation. Therefore, the origins are different, discussed later.

3.2. Isochronal annealing

Isochronal annealing experiment has been done after saturation implantation with dual H^+ and D^+ ions. The fractions of H and D retained are shown as a function of temperature in Fig. 2. It is seen from Fig. 2 that there exist two re-emission stages; a stage at 363 K and a broad stage at 573 ± 100 K. The thermal annealing curves correspond essentially with that of D obtained after the independent D^+ implantation [13]. In Fig. 2, it is seen that the decay rate of H is the same as that of D at the lower temperature stage and is faster than that of D at the higher temperature stage, which it is so-called isotope effect in the thermal re-emission of H and D retained in beryllium.

4. Discussion

4.1. Retention

As seen from Fig. 1, the steady state concentrations of hydrogen isotopes retained are extremely high. This fact indicates that the trapping rate constant Σ_T^i for mobile hydrogen species i is extremely high compared with other rate constants related to the re-emission, namely, the molecular recombination rate constant K_1^{ii} and the detrapping rate ${\sigma_d}^i\phi^i$, where ${\sigma_d}^i$ is the ion-induced detrapping cross-section and ϕ^i is the ion flux and that all the trapping sites are fully occupied. The latter fact is simply estimated from kinetic considerations of the local concentrations at steady state of mobile and trapped hydrogen species n^i and n_T^i, respectively,

$$\phi^i/\Delta R^i = 2K_1^{ii}(n^i)^2 \quad \text{(steady state)}, \tag{1}$$

$$\Sigma_T^i(C_0 - n_T^i)n^i = {\sigma_d}^i\phi^i n_T^i \quad \text{(local equilibrium)}, \tag{2}$$

where i represents a hydrogen species (i = H, D or T), ΔR^i is the range straggling and C_0 is the trap density. Since it was experimentally found from the change of ERD spectra that the re-emission rate at each re-emission stage was independent of the depth [13], the local molecular recombination between mobile species was taken into account for re-emission processes. The re-emission processes were assumed to be the same in the bulk as in the oxidized layers.

For a solution of the two equations, the concentration of hydrogen retained at steady state is given by the following equation:

$$n_T^i = \frac{C_0^i}{{\sigma_d}^i\sqrt{\phi^i\Delta R^i C_0^i}\sqrt{(K_1^{ii})/\left((\Sigma_T^i)^2 C_0^i\right)} + 1}, \tag{3}$$

where $\phi^i \sim 4 \times 10^{17}/\mathrm{m}^2 \cdot \mathrm{s}$ and $\Delta R^i \approx 2 \times 10^{-8}$ m in this study. The other rate constants are not available for beryllium, but for graphite, namely $K_1^{ii}/(\Sigma_T^i)^2\ C_0 \approx 1$ [17] and ${\sigma_d}^i \sim 3 \times 10^{-22}$ m^2 [18]. According to the diffusion-limited reaction model, it is assumed that $\Sigma_T^H = 4\pi r_T D^H \eta^H$ and $\Sigma_T^D = 4\pi r_T D^D \eta^D$ where r_T is the effective radius for trapping, D^i is the diffusion constant of i species, η^i is the trapping probability for i species and that $K_1^{HH} = 4\pi r_R^{HH} D^H \xi^{HH}$ and $K_1^{DD} = 4\pi r_R^{DD} D^D \xi^{DD}$ where r_R^{ij} are the effective radii for recombination between mobile species i and j and ξ^{ij} are the formation probability for a molecule ij. Thus, the ratio of $K_1^{ii}/(\Sigma_T^i)^2 C_0$ is not dependent on D^i, but r_T, r_R^{ij}, η^i and ξ^{ij} namely almost independent of materials. Therefore, the first term of the denominator of Eq. (3) was estimated to be 6×10^{-3} for $C_0 \sim 5 \times 10^{28}/\mathrm{m}^3$, using the data for graphite. This fact indicates that the saturation concentration is equal to the trap density. Since the trap for hydrogen in beryllium is accepted to be lattice defects induced by ion irradiation, the isotope difference is ascribed to the difference between the d.p.a. (displacement per atom) rates of beryllium by H^+ and D^+ ions. When the power-law approximation is used for the Thomas–Fermi interaction potential for elastic collision of Be-hydrogen, the D/H ratio of the values of d.p.a. by D^+ and H^+ ions is proportional to $(M_H/M_D)^m$ ($m = 1/3$), which is very consistent with the experimental one.

The concentrations of H and D retained at steady state on simultaneous H^+ and D^+ irradiation are calculated from two sets of the equations for H and D for 'steady state' and 'local equilibrium', in which the rate constants K_1^{ij} of mixed molecular recombination and the ion-induced detrapping cross-sections ${\sigma_d}^{ij}$ due to mixed recoil collisions are taken into account additionally. When $\phi^{\mathrm{H}} = \phi^{\mathrm{D}}$, the ratio of $n_{\mathrm{T}}^{\mathrm{H}}/n_{\mathrm{T}}^{\mathrm{D}}$ is expressed by the following equation [19]:

$$\frac{n_{\mathrm{T}}^{\mathrm{H}}}{n_{\mathrm{T}}^{\mathrm{D}}} = \sqrt{\frac{K_1^{\mathrm{DD}}\left(\sigma_{\mathrm{d}}^{\mathrm{D}}/\Sigma_{\mathrm{T}}^{\mathrm{D}}\right)^2}{K_1^{\mathrm{HH}}\left(\sigma_{\mathrm{d}}^{\mathrm{H}}/\Sigma_{\mathrm{T}}^{\mathrm{H}}\right)^2}} \times \left(\sqrt{1 + \frac{(1-f)^2}{16}\frac{\left(K_1^{\mathrm{HD}}\right)^2}{K_1^{\mathrm{HH}}K_1^{\mathrm{DD}}}} - \frac{(1-f)}{4}\frac{K_1^{\mathrm{HD}}}{\sqrt{K_1^{\mathrm{HH}}K_1^{\mathrm{DD}}}}\right), \tag{4}$$

where $f = \Delta R^{\mathrm{D}}/\Delta R^{\mathrm{H}}$ which is 1.25 in this study, $\sigma_{\mathrm{d}}{}^{\mathrm{H}} = \sigma_{\mathrm{d}}{}^{\mathrm{HH}} + \sigma_{\mathrm{d}}{}^{\mathrm{DH}}$, $\sigma_{\mathrm{d}}{}^{\mathrm{D}} = \sigma_{\mathrm{d}}{}^{\mathrm{DD}} + \sigma_{\mathrm{d}}{}^{\mathrm{HD}}$. According to the diffusion-limited reaction model, it is assumed that $K_1^{\mathrm{HD}} = 4\pi r_{\mathrm{R}}^{\mathrm{HD}} D^{\mathrm{HD}} \xi^{\mathrm{HD}}$, where r_{R}^{ij} are the effective radii for recombination between mobile species i and j, expressed by $2\sqrt{(D^i + D^j)\tau}$, here τ is the characteristic time, ξ^{ij} are the formation probability for a molecule ij and $D^{\mathrm{HD}} = (D^{\mathrm{H}} + D^{\mathrm{D}})/2$. Thus, $(K_1^{\mathrm{HD}})^2/K_1^{\mathrm{HH}} \cdot K_1^{\mathrm{HH}} = \sqrt{(D^{\mathrm{D}}/D^{\mathrm{H}})^3 (1 + D^{\mathrm{H}}/D^{\mathrm{D}})^3/8}$. Since the isotope ratio of $K_1^{ij}(\sigma_{\mathrm{d}}{}^{i}/\Sigma_{\mathrm{T}}^{i})^2$ is almost independent of materials, as discussed above, the data for graphite may be applicable to Eq. (4). In such a case, the ratio $n_{\mathrm{T}}^{\mathrm{D}}/n_{\mathrm{T}}^{\mathrm{H}}$ is estimated to be 1.25, which is very consistent with the experimental one.

4.2. *Isochronal annealing*

In Fig. 2, two re-emission stages were observed as a previous result on the independent irradiation of D^+ ion [13]. The ERD spectra showed three emission stages; the broad stage is divided into two stages from the oxidized surface layers and from the projected range in the bulk. The re-emission curve on the simultaneous H^+ and D^+ irradiation in Fig. 2 indicates that there exists no isotope difference at the lower temperature stage, at which the re-emission was speculated to take place due to thermal dissociation of linear chain clusters of Be-dihydride molecule. On the simultaneous H^+ and D^+ irradiation, clusters of mixed Be-dihydride molecule are formed. Since Be-dihydride is unstable, no isotope difference is concluded to indicate that the lower temperature stage takes place due to thermal break-up of the Be–Be bonds in the chain clusters. The two higher temperature stages are also concluded to take place due to thermal detrapping of individual hydrogen species from the trapping sites.

5. Summary

The concentration profiles of H and D retained in beryllium by simultaneous and independent irradiations of H^+ and D^+ ion beams at room temperature and on post isothermal annealing have been measured by means of ERD and RBS techniques.

It has been found on the simultaneous irradiation that the D/H ratio of the concentrations of H and D retained at steady state is 1.2 ± 0.1. The isotope ratio is in good agreement with the theoretical one calculated from the kinetic equations for free and trapped hydrogen species at steady state and local equilibrium in which the diffusion-limited rate constants for the trapping local molecular recombination and ion-induced detrapping cross-section are take into account. In the calculation, data on carbon were used because data on beryllium are not available. Finally, it is noted that the experimental data on the rate constants of elementary processes for beryllium are needed.

References

[1] The JET Team, J. Nucl. Mater. 196–198 (1992) 3.

[2] The TFTR Group, Proc. of 11th Int. Conf. Plasma Surface Interactions in Controlled Fusion Devices, Mito, Japan, May 23–27, 1994, to be published.

[3] W. Möller, J. Nucl. Mater. 162–164 (1989) 138.

[4] R.A. Causey, J. Nucl. Mater. 162–164 (1989) 151.

[5] K.L. Wilson et al., Nucl. Fusion 1 (Suppl.) (1991) 31.

[6] W. Möller, B.M.U. Scherzer, Appl. Phys. Lett. 50 (1987) 1870.

[7] A.A. Haasz, P. Franzen, J.A. Davies, S. Chiu, C.S. Pitcher, J. Appl. Phys. 77 (1995) 66.

[8] K. Morita, Y. Hasebe, Mem. Fac. Eng. Nagoya Univ. 45 (1993) 57.

[9] W.R. Wampler, J. Nucl. Mater. 122&123 (1984) 213.

[10] W.R. Wampler, J. Nucl. Mater. 196–198 (1992) 983.

[11] H. Kawamura et al., J. Nucl. Mater. 176&177 (1990) 66.

[12] W. Möller, B.M.U. Scherzer, J. Bohdansky, IPP-JET Report No. 26, 1986.

[13] B. Tsuchiya, K. Morita, J. Nucl. Mater. 233–237 (1996) 898; 1213.

[14] S. Mizusawa, R. Sakamoto, T. Muroga, N. Yoshida, presented at 7th Int. Conf. on Fusion Reactor Materials (ICFRM-7), Obninsk, Russia, Sept. 25–29, 1995.

[15] B. Tsuchiya, K. Morita, J. Nucl. Mater. 227 (1996) 195.

[16] S. Nagata, Nucl. Instrum. Methods B6 (1985) 533.

[17] K. Morita, Y. Muto, J. Nucl. Mater. 196–198 (1992) 963.

[18] B. Tsuchiya, K. Morita, J. Nucl. Mater. 226 (1995) 298.

[19] K. Morita, B. Tsuchiya, these Proceedings, p. 27.