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Tritium permeation study through tungsten and nickel using pure tritium ion beam

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Abstract

Permeation behavior of tritium (T) implanted into tungsten and nickel has studied by using pure tritium ion beam. Tritium permeation characteristics of steady and transient states were obtained and were compared with the result of deuterium (D) under the same experimental conditions. It was concluded from the steady state results of T and D that the permeation was controlled by diffusion in implantation side – diffusion in permeation side process for tungsten and recombination at the implantation surface – diffusion in the permeation side process for nickel. Effective diffusivities were evaluated from the permeation behavior of pure T and D. Isotope effect on the diffusivity between D and T did not agree with the classical diffusion theory, but could be explained by a quantum statistical diffusion model for nickel. The results indicated that diffusivity of T could be larger than that of D in W and Ni, respectively.

Keywords: Tritium; Permeation; Diffusion; Isotope effect; Tungsten; Nickel

1. Introduction

In a DT fusion reactor, estimation of tritium permeation amount into the primary coolant is one of critical issues from a viewpoint of safety evaluation. It is generally known that hydrogen isotopes particles in DT plasma implanted into plasma facing components (PFCs) increase tritium permeation rate (plasma driven permeation (PDP)). Therefore, a number of studies [1–4] have carried out for the PDP in order to estimate the tritium permeation in the fusion reactor. To evaluate tritium permeation amount accurately, it is essential to establish database for tritium transport behavior in materials and to know how tritium behavior in materials differs from that of protium or deuterium. There are, however, quite few reports on the PDP of tritium except for some studies by Causey [1], and further database of tritium is significantly desired. The authors have studied the tritium and deuterium permeation behavior using an experimental apparatus named tritium permeation apparatus (TPA), which can produce pure tritium ion beam with low energy region [5–7]. Principle purpose of our study is to obtain the PDP characteristics of pure tritium implanted into PFC materials under the simulated plasma conditions. A series of data for tritium allows us to verify the difference of permeation or diffusion behavior with deuterium, and to estimate the tritium behavior under the variety of conditions with relatively rich deuterium data.

This report presents the permeation behavior of pure tritium implanted into tungsten as a promised metal for PFC of ITER and of future fusion devices, and that implanted into nickel selected as a reference metal for the study of isotope effect because permeation behavior of protium and deuterium into nickel are well investigated. Based on obtained results, isotope effect on permeation and diffusion behaviors of tritium and deuterium is discussed.

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2. Experimental

The permeation experiments were carried out with foils of W (promised material of ITER-PFC [8]) and Ni (the fundamental metal). The W foil was 99.5% purity and 50 μm thick, and annealed at 1273 K in vacuum furnace for 3 h. The Ni foil (as received) was 0.1 mm thick, and purity was 99.7%. T^+ (>95% isotope purity) with 1 keV energy was implanted onto metal specimen each condition that specimen temperature and ion flux were constant. The amount of tritium permeated through specimen was measured by a quadropole mass spectrometer. A series of permeation experiments were performed by changing specimen temperature and incident ions flux. The deuterium permeation experiment was also carried out with the same procedure to achieve accurate comparative data.

3. Results and discussions

3.1. Steady state permeation behavior

Fig. 1 shows the temperature dependence of the steady state permeation flux of pure tritium (T) and deuterium (D) implanted into W and Ni, respectively. In the case of W, the data has an appreciable large scattering; no systematic difference between D and T is observed. The permeation of D and T implanted into W is almost constant against the specimen temperature. On the other hand, the permeation of D and T implanted into Ni has clear temperature dependence, and slight difference between T and D can be observed in the permeation flux. Clear difference on the activation energy on the permeation between D and T was not observed for Ni, the activation energies of steady state permeation of D and T are 31.3 ± 2.2 and 32.5 ± 1.4 kJ/mol in the range below 550 K, respectively. The observed permeation behavior for W and Ni such as difference of temperature dependency and difference of absolute value of the permeation flux between D and T could be attributed to the difference of the rate determining process of the steady state permeation. In accordance with the steady state transport model proposed by Doyle and Brice [9], the hydrogen transport process implanted into metals can be classified into four categories by the combining the rate determining process (the recombination reaction on the surface: R-control or diffusion process: D-control) in each region divided by ion range of hydrogen (implantation or permeation side): (1) R-control on both surfaces (RR regime); (2) the R-control on the implantation surface and D-control in the permeation side (RD regime); (3) D-control in both sides (DD regime); and (4) D-control in the implantation side and R-control on permeation surface (DR regime). The permeation flux (ϕ_p) of the each category can be expressed by the equations summarized in Table 1.

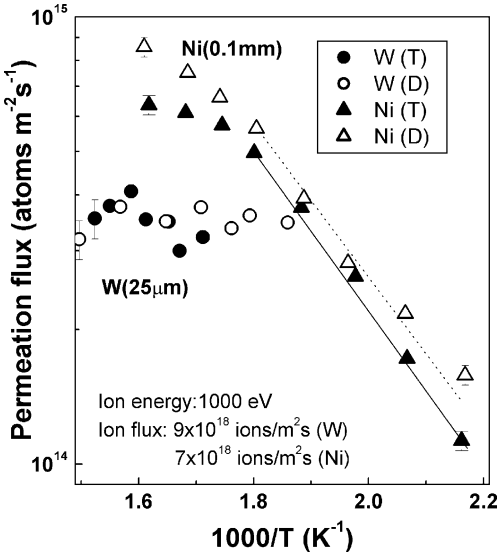

Fig. 1. Temperature dependence of the steady state permeation flux of pure T and D implanted into W and Ni.

As to the incident flux dependence of the steady state permeation, the results showed the almost proportional relationship between the incident flux and the permeation flux for W, and showed almost proportional relationship between square root of the incident flux and the permeation flux for Ni in lower temperature below 550 K as shown in Fig. 2. Concerning the results of present experiments and the previous knowledge on permeation behavior of W, where the permeation increases with the ion range [5], the rate determining process of steady state permeation of T and D for individual metal was estimated to be DD regime for W, and RD regime for Ni below 550 K, respectively based on the above model.

Table 1
Four rate determining process and those expressions of hydrogen transport model by Doyle and Brice [9]

Category	Expression
RR	$\phi_p = \frac{kr_b}{kr_b + kr_f}\alpha\phi_i$
DD	$\phi_p = \frac{R_p D_b}{dD_f}\alpha\phi_i$
RD	$\phi_p = \frac{D_b}{d\sqrt{kr_f}}\sqrt{\alpha\phi_i}$
DR	$\phi_p = \frac{R_p^2 kr_b}{D_f}(\alpha\phi_i)^2$

D – diffusivity, kr – recombination coefficient, R_p – ion range, d – membrane thickness, ϕ_p – permeation flux, ϕ_i – implantation flux, α – implantation probability. Subscript f and b means implantation and permeation side, respectively.

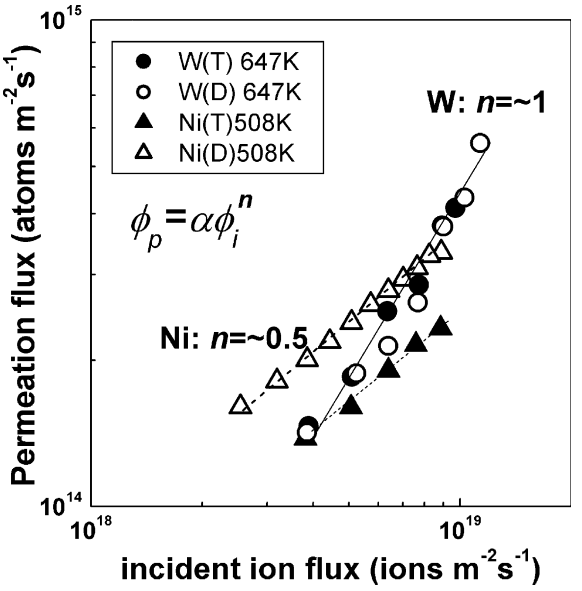

Fig. 2. Incident flux dependence of the steady state permeation flux of pure T and D implanted into W and Ni. ϕ_p and ϕ_i are permeation flux and incident flux, respectively, and α is constant in this figure.

3.2. Transient and steady state permeation analysis

The rate determining process of tritium permeation through each metal was determined in Section 3.1. Since the steady state permeation was found to be controlled by diffusion process in permeation side for W and Ni, the boundary condition of the permeation side surface can be simplified. In order to clarify the isotope effect on transport process such as diffusion process, numerical analysis of transient and steady state permeation behavior was carried out for W and Ni with TMAP code [10]. The analysis was carried out by solving following basic diffusion equation with the boundary condition of individual rate determining process of the permeation,

$$\frac{\partial C(x,t)}{\partial t} + \nabla J(x,t) = S(x,t) - \frac{\partial C_T(x,t)}{\partial t}, \quad (1)$$

where $C(x,t)$ – hydrogen isotope concentration, $J(x,t)$ – diffusion flux of hydrogen isotopes, $S(x,t)$ – source of hydrogen isotopes, $C_T(x,t)$ – trapped hydrogen isotopes concentration.

The boundary conditions are expressed as

$$C(0,t) = C(d,t) = 0, \quad \text{for W (DD regime)}, \quad (2)$$

$$D_f \frac{\partial C(0,t)}{\partial x} = kr_f C(0,t)^2$$
$$\text{and } C(d,t) = 0, \quad \text{for Ni (RD regime)}, \quad (3)$$

where d is thickness of metal, kr is recombination coefficient, D is diffusivity and subscript f means implantation side.

In the analysis, existence of two layers with different effective diffusivity (D_f in implantation side and D_b in permeation side) divided by the ion range was considered, and so called trapping phenomena in the materials were neglected, because the previous investigations on deuterium permeation through annealed W [6] and Ni [2] indicated that strong trap site could not exist in both metals. The ion range (R_p) was evaluated to be around 10 nm both for W and Ni by TRIM98 code [11]. Implantation flux was assumed to be $S(x,t) = \phi_i \delta(x - R_p)$ by assuming implantation probability (α) to be unity. D_f, D_b for each metal and kr for Ni were parameters to tie the analysis results to the experimental observations.

The TMAP analysis showed that the transient behavior was controlled only by D_b due to the short R_p of around 10 nm in comparison with the specimen thickness (25 μm of W and 0.1 mm of Ni), and that D_f and kr controlled the tendency of the temperature and incident flux dependence of the steady state permeation. Figs. 3 and 4 show the example of transient analysis of the permeation of D and T implanted into W and Ni, respectively. In these figures, the good agreement between observed permeation and TMAP simulation can be seen. Fig. 5 shows the derived D_b of T and D in W and Ni together with the diffusivity reported by previous investigators [2,3,12–17]. It can be seen in Fig. 5 that the derived D_b of D and T in Ni are almost the same as that for the previous work. On the other hand, the derived D_b in W is smaller than previous work. The derived D_b in W can be considered as an effective diffusivity (D_{eff}) containing substantial trap effect, which can not be distinguished from the reduce of diffusivity [6], and it can be expressed in the following equation [18]:

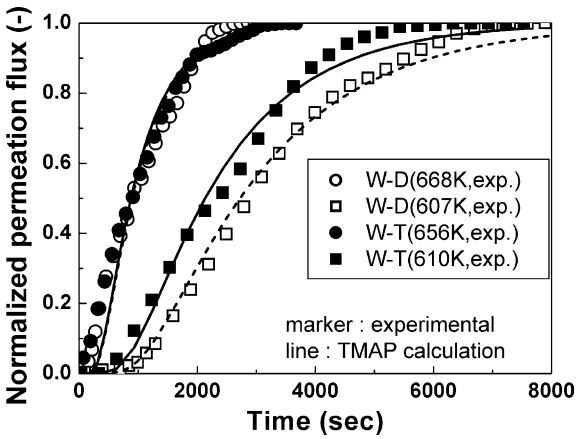

Fig. 3. Obtained transient permeation behavior data of D and T implanted into W and analytical curves by TMAP code with the DD regime boundary condition.

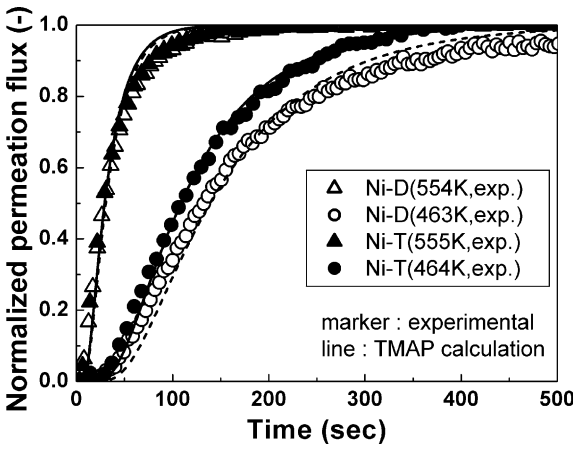

Fig. 4. Obtained transient permeation behavior data of D and T implanted into Ni and analytical curves by TMAP code with the RD regime boundary condition.

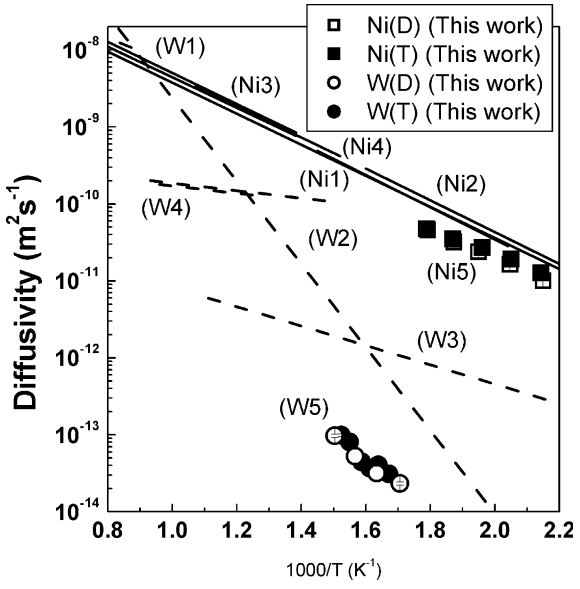

Fig. 5. Effective diffusivity of pure T and D in W and Ni. (W1) H in W [12], (W2) H in W [13], (W3) H in W [14], (W4) H, D in W [15], (W5) D, T in W (this work), (Ni1) D in Ni [2], (Ni2) D in Ni [3], (Ni3) D, T in Ni [16], (Ni4) D in Ni [17], and (Ni5) D, T in Ni (this work).

$$D_{\mathrm{eff}} = D \Big/ \left(1 + \frac{C_{\mathrm{T}}}{C_{\mathrm{T0}}} \exp\left(\frac{E_{\mathrm{T}}}{kT}\right)\right), \tag{4}$$

where D – diffusivity, C_{T} – trapped concentration, C_{T0} – trapping site density, E_{T} – trap energy, k – Boltzmann constant, and T – absolute temperature.

For the isotope effect on D_{b}, slight difference between T and D was observed in both W and Ni. On the other hand, the analytical result indicates that derived D_{f} is about several times larger than D_{b} for both W and Ni. Similar behavior has observed for Cu also [7], and this enhancement of D_{f} could be attributed to the ion implantation such as creation of short path or decrystallization. Although detail mechanism of enhancement of D_{f} is under investigation, this assumption can describe the permeation behavior at steady and transient state for both RD and DD regime.

3.3. Isotope effect on diffusivity

Based on the obtained results shown in Fig. 5, the isotope effect on diffusivity was theoretically considered.

In accordance with the classical diffusion theory (CDT) [19], the isotope effect on diffusivity can be expressed by

$$D^{\alpha}/D^{\beta} = \sqrt{m^{\beta}/m^{\alpha}}, \tag{5}$$

where m^{α} and m^{β} mean mass of isotope α and β, respectively.

However, some of reports suggested that the isotope effect on diffusivity is disagreed with the CDT [16,17,20]. Therefore, the modified quantum statistical diffusion theory was proposed by Ebisuzaki or Katz for fcc metals [16,20].

In the Ebisuzaki model, the isotope effect of D can be expressed by

$$\frac{D^{\alpha}}{D^{\beta}} = \sqrt{\frac{m^{\beta}}{m^{\alpha}}} \left(\frac{g\left(\theta/\sqrt{\beta}T\right)}{g\left(\theta/\sqrt{\alpha}T\right)}\right)^{3} \left(\frac{g\left(\theta^{*}/\sqrt{\alpha}T\right)}{g\left(\theta^{*}/\sqrt{\beta}T\right)}\right)^{2}, \tag{6}$$

where $g(x) \equiv (2/x)\sinh(x/2)$, θ – characteristic vibration temperature, ($\theta = h\nu/k$, $\theta^{*} = h\nu^{*}/k$), h – Planck constant, k – Boltzmann constant, ν and ν^{*} are vibration frequency at ground and excited state for diffusion, respectively.

Fig. 6 shows the obtained ratio of D_{b} of D and T in W and Ni with previous studies and also with studies on bcc metals (Nb, Ta) and fcc metal (Ni, Pd). Observed isotope effect on the D_{b} in W (bcc) and Ni (fcc) are not agreed with the CDT, but qualitative temperature dependence of D_{b} agrees with the reported isotope effect on diffusivity in fcc and bcc metals.

Since Ebisuzaki's diffusion model shown in Eq. (6) can be applied to fcc metal, the isotope effect of diffusion in Ni was examined to explain using this model. As a result, the isotope effect on D_{b} in Ni can be described by this model using $\theta = \sim 1325$ K and $\theta^{*} = \sim 2780$ K. Derived θ and θ^{*} are near to reported value for Ni ($\theta = 1350$–1450 K and $\theta^{*} = 2300$–2660 K) [16,20].

It was observed in the present work for Ni in the temperature region below 560 K that D_{b} for T was larger than D_{b} for D. Although Ebisuzaki reported this phenomenon only in the low temperature region below 360 K [22], present result is similar to the characteristics of

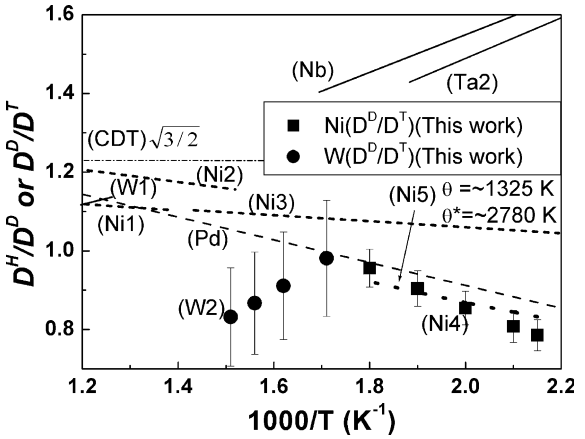

Fig. 6. Ratio of $D^D_{\text{eff}}/D^T_{\text{eff}}$ in W and Ni and comparison of previous reports on isotope effect on diffusivity in fcc and bcc metals. (Ni1) D/T–Ni [16], (Ni2) H/D–Ni [17], (Ni3) H/D–Ni [20], (Ni4) D/T–Ni (this work), (Ni5) D/T–Ni (predicted value by Ebisuzaki model at $\theta = \sim 1325$ K, $\theta^* = \sim 2780$ K), (W1) H/D in W [15], (W2) D/T–W (this work), (Pd) H/T–Pd [21], (Nb) H/D–Nb [21], (Ta) H/D-Ta [21], and (CDT) D/T by classical diffusion theory.

Pd (fcc metal) that the diffusivity of T is larger than that of D in the temperature region below 550 K [21].

As to the isotope effect of diffusivity in W, D_{eff} consists of diffusivity and trap effect as shown in Eq. (4). Therefore, both of diffusion and trapping can be expected as the origin of isotope effect in D_{eff}. Esteban et al. [15] reported larger isotope effect on trapping than that on diffusion in D_{eff} in W. Therefore, when it is considered that the derived D_{eff} in W has isotope effect, obtained isotope effect shown in Fig. 6 could be attributed to the trapping effect shown in Eq. (4). However, the data for the isotope effect on D_{eff} is still limited, and further database for trap free diffusion in W is necessary to discuss on it.

4. Conclusions

Permeation behavior of tritium implanted into tungsten (W) as a candidate of plasma facing materials and nickel (Ni), as a fundamental metal, has studied by using pure tritium ion beam as a study to estimate the tritium permeation amount in the fusion reactors, and following results were obtained:

(1) The rate determining process of the pure tritium permeation was determined as DD regime for W and RD regime for Ni below 550 K.
(2) Diffusivity of pure tritium has been determined for W and Ni by the analysis of obtained transient and steady state behavior. The diffusivity of tritium in Ni is almost the same as that of protium or deuterium by the previous work. On the other hand, the diffusivity in W is smaller than previous work with protium or deuterium. It could be attributed the trap effects containing in it.
(3) Observed isotope effects on diffusion between tritium and deuterium for both W and Ni are not agreed with classical diffusion theory, and present results indicated that the diffusivity of tritium could be larger than that of deuterium. For observed isotope effect for Ni, there exists the possibility that it could be explained by the existing modified diffusion model.

Further experimental and theoretical studies of isotope effect on the tritium transport in materials will be carried out to contribute to the R&D of the fusion reactors in a viewpoint of tritium safety.

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