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Journal of Nuclear Materials 297 (2001) 285–291

Journal of  
nuclear  
materials

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# Tritium permeation behavior implanted into pure tungsten and its isotope effect

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Received 12 August 2000; accepted 26 May 2001

## Abstract

A first tritium permeation experiment with pure tungsten specimen, which was 25  $\mu\text{m}$  thick, and annealed at 1273 K for 3 h, was successfully carried out using pure tritium ion beam. The deuterium permeation experiment was also carried out using the same tungsten specimen. The permeation of deuterium and tritium at steady state was found to be controlled by diffusion at implantation side and permeation side (DD regime). No significant isotope effect was observed on the steady-state permeation behavior between deuterium and tritium. On the other hand, the isotope effect on the effective diffusion coefficient in tungsten, derived from the analysis of transient permeation behavior, was observed between deuterium and tritium. The result indicates tritium has larger activation energy of effective diffusion than deuterium. It was not inconsistent with the reported isotope effects of diffusion coefficient for bcc metal, to which tungsten belongs. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 28.52.Fa

## 1. Introduction

In a deuterium (D)–tritium (T) fusion reactor development, knowledge of tritium behavior in and out of a fusion facility is one of the key issues. Especially, estimation of permeation amounts of tritium to coolant through plasma facing components is important in order to establish its safety evaluation method. It is known that the permeation of hydrogen isotopes through metal by plasma exposure or by ion implantation is greatly enhanced compared to that by gas exposure under the same incident particle flux condition. These phenomena are referred to as plasma driven permeation (PDP), implantation driven permeation (IDP) and gas driven permeation (GDP), respectively. From the viewpoint of

safety of fusion reactors, it is important to know thoroughly about tritium permeation through plasma facing components, and thus various experiments concerned with the PDP [1–3] and IDP [4–7] have been performed.

Though many of the above studies were performed using deuterium or hydrogen, there are only a few reports on IDP or PDP with tritium, such as those on PDP by Causey et al. [2] by discharge methods, and tritium retention work by Yamaguchi et al. [8] using ion gun. In addition, even these studies were performed using tritium swamped by deuterium or hydrogen.

Authors have investigated the IDP behavior of deuterium implanted into tungsten and other metals [9–11] in order to obtain knowledge on the permeation mechanism using a tritium permeation apparatus (TPA) [12] at Tritium Process Laboratory (TPL) of Japan Atomic Energy Research Institute (JAERI) [13]. The production of pure tritium ion beam was then successfully carried out with the TPA, and the first tritium permeation experiment was performed for pure tungsten, which is one of the candidate materials for divertor plates for Inter-

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national Thermo-nuclear Experimental Reactor (ITER). In this report, the permeation behavior of tritium through tungsten is presented, and the isotope effect on the permeation behavior between tritium and deuterium is discussed.

## 2. Experimental

### 2.1. Apparatus

The TPA [12] consists of the following five sub-systems: (1) an ion source for production of a hydrogen isotope ion beam with high flux and low energy, (2) an ion implantation chamber system, (3) a measuring system of the permeated gases through the target, (4) tritium supply and recovery system, and (5) a vacuum pump system. The whole system has been installed in a glovebox of TPL at JAERI. The schematic diagram of tritium permeation apparatus is shown in Fig. 1.

The ion source is a modified quartz capillary duo-PIGatron in order to produce low energy ions with high intensity designed by Isoya [14]. More than 90% of the ion species in the extracted beams was confirmed to be atomic ion by means of mass spectrometry. The other species were di-atomic and tri-atomic ions. The monochromatic atomic ion energy can be varied from 100 eV to 2 keV. The effective implantation area of the target is 25 mm in diameter. Tritium supply and recovery system of the TPA consists of two zirconium–cobalt beds (for supply and recovery), a reservoir tank (3 l in volume) and a pressure measuring system. Permeation fluxes are measured by a quadrupole mass spectrometer ( $M/e = 4$  for  $D_2$  and  $M/e = 6$  for  $T_2$ ), calibrated by the capillary method using  $D_2$  and  $T_2$ , respectively. The permeation flux is determined from the increase of the above mass peaks. The base pressure of upstream chamber is

maintained below  $3 \times 10^{-6}$  Pa by a cryo-pump. The gas pressure of the upstream (incident) side in the main chamber is controlled at around  $4 \times 10^{-4}$  Pa during the experiment. The base pressure of the down-stream (permeation) side is kept below  $1 \times 10^{-5}$  Pa during the experiment by an ion-pump.

### 2.2. Samples and permeation experiment

Pure tungsten (>99.5%) metal sample from Nilaco corporation was cut into discs of 34 mm $\varnothing$  from a foil of 25  $\mu$ m thick to be used as the target for the permeation experiments. Major impurities in the tungsten foil were Mo(150 ppm), Pb and Si(<50 ppm), respectively. A sample foil was annealed at 1273 K for 3 h in a vacuum furnace before the experiment. The permeation experiment was carried out with deuterium ion beam at first and then with tritium ion beam without replacing the target specimen: both the deuterium permeation characteristics and tritium permeation characteristics were investigated with the same tungsten specimen.

The deuterium experiment was carried out by the following method. The specimen was heated up to about 670 K for several hours under vacuum for degassing after clamping on the target flange. Pre-implantation with the deuterium ions was then carried out at about 660 K until the permeation flux became constant. After these preparations, the permeation characteristic measurement was performed, where the constant energy deuterium ions were implanted into the constant temperature specimen with constant ion flux. The permeation flux was measured by a quadrupole mass spectrometer (QMS) scanning the mass number 3–6. The implantation was continued until the permeation flux reached steady state. The permeation flux was measured even after the implantation was terminated until it reached the base value. A series of permeation

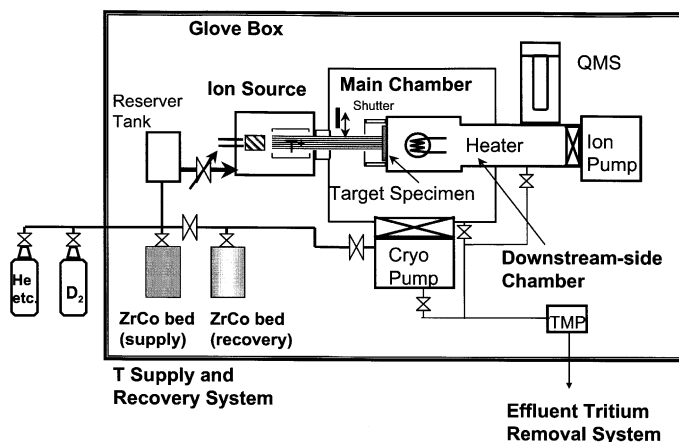


Fig. 1. Schematic diagram of the TPA.

experiments were performed as a function of target temperature, incident ions flux and incident ion energy.

The tritium experiment was performed with the same procedure as the deuterium experiment except for using tritium gas (>95% purity) instead of deuterium gas. Tritium was loaded to the reservoir tank from the Zr–Co supply bed. Total usage of tritium gas at the present tritium experiment was about 0.26 PBq (7100 Ci). Almost all the tritium gas introduced into ion source was evacuated by a cryo-pump, and was recovered into the Zr–Co recovery bed by a regeneration of the cryo-pump after experiment.

### 3. Results and discussions

Fig. 2 shows typical traces of tritium permeation flux measured in the present experiment. More than 90% of the permeated tritium was released in the form of  $T_2$ . The permeation behavior was analyzed both at steady state and transient state.

#### 3.1. Permeation behavior at steady state

Figs. 3(a)–(c) show the parameter dependence of the steady-state permeation behavior of D and T implanted into pure tungsten. Dependencies of the permeation flux of D and T on temperature, incident ion flux and incident ion energy are shown in Figs. 3(a)–(c), respectively. Where, the incident ion energy was converted to mean projected range of D and T in tungsten, which was derived TRIM calculation [15].

The value and the parameter dependencies of the permeation flux of D and T observed in the present experiment were similar to each other as shown in Figs. 3(a)–(c). Permeation fluxes of D and T were found to be

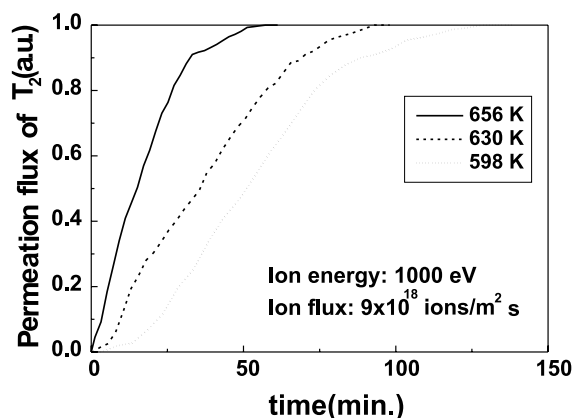


Fig. 2. Typical IDP traces measured at the experiment, where the tritium ions were implanted into pure tungsten at various temperatures.

nearly constant and independent of the specimen temperature as shown in Fig. 3(a). The permeation fluxes of D and T were almost proportional to the incident ion flux as shown in Fig. 3(b). And  $n$  values, which were determined from the following relationship:  $\phi_p = k\phi_i^n$ , where  $\phi_p$  is the permeation flux,  $\phi_i$  is the incident flux, and  $k$  is the constant, were found to be 1.24 and 1.12 for D and T, respectively. Permeation fluxes of D and T were found to increase with increase of the mean projected range as shown in Fig. 3(c).

The rate-determining process of the permeation of D and T through pure tungsten was discussed from the results of the steady-state permeation characteristics. From the steady-state hydrogen transport model proposed by Doyle and Brice [16,17], the permeation process of hydrogen isotopes implanted into metals can be classified into four categories depending on whether the rate-determining step is the recombination reaction on the surface or diffusion process for hydrogen isotopes, at the front or back side of the metal. These are (1) recombination reaction at both sides (RR regime), (2) the recombination at the front side surface and diffusion in the back side (RD regime), (3) diffusion in both sides (DD regime) and (4) diffusion in the front side and recombination at back side (DR regime). The permeation flux equation for each of the above regimes is listed in Table 1 with parameter dependence. By comparing the parameter dependencies of the predicted permeation characteristics with parameter dependencies of observed steady-state permeation behavior, it is possible to estimate the rate-determining process of steady-state permeation of D and T through pure tungsten. Because the experimental results showed that (1) the permeation is almost constant and independent of specimen temperature, (2) the permeation is almost proportional to incident ion flux, and (3) the permeation increases with increase of ion energy, which corresponds to the increase of range, it is appropriate to classify these permeation behavior into the DD regime as shown in Table 1, in the case where it is assumed the activation energy of the diffusion coefficient in the implanted side and bulk is equal. These results agree with the previous results of the permeation behavior of the deuterium implanted into unannealed tungsten [10].

From the discussion of the steady-state permeation characteristics, it is concluded that the permeation of D and T through pure tungsten at steady state is controlled by the DD regime, and this result agreed with the prediction by the model for tungsten [16,17].

As to the isotope effect of steady-state permeation, no significant difference between D and T on the steady-state permeation behavior was observed. When the permeation is controlled by DD regime, the isotope effect of diffusion coefficient on the permeation flux is canceled out between the diffusion coefficient at

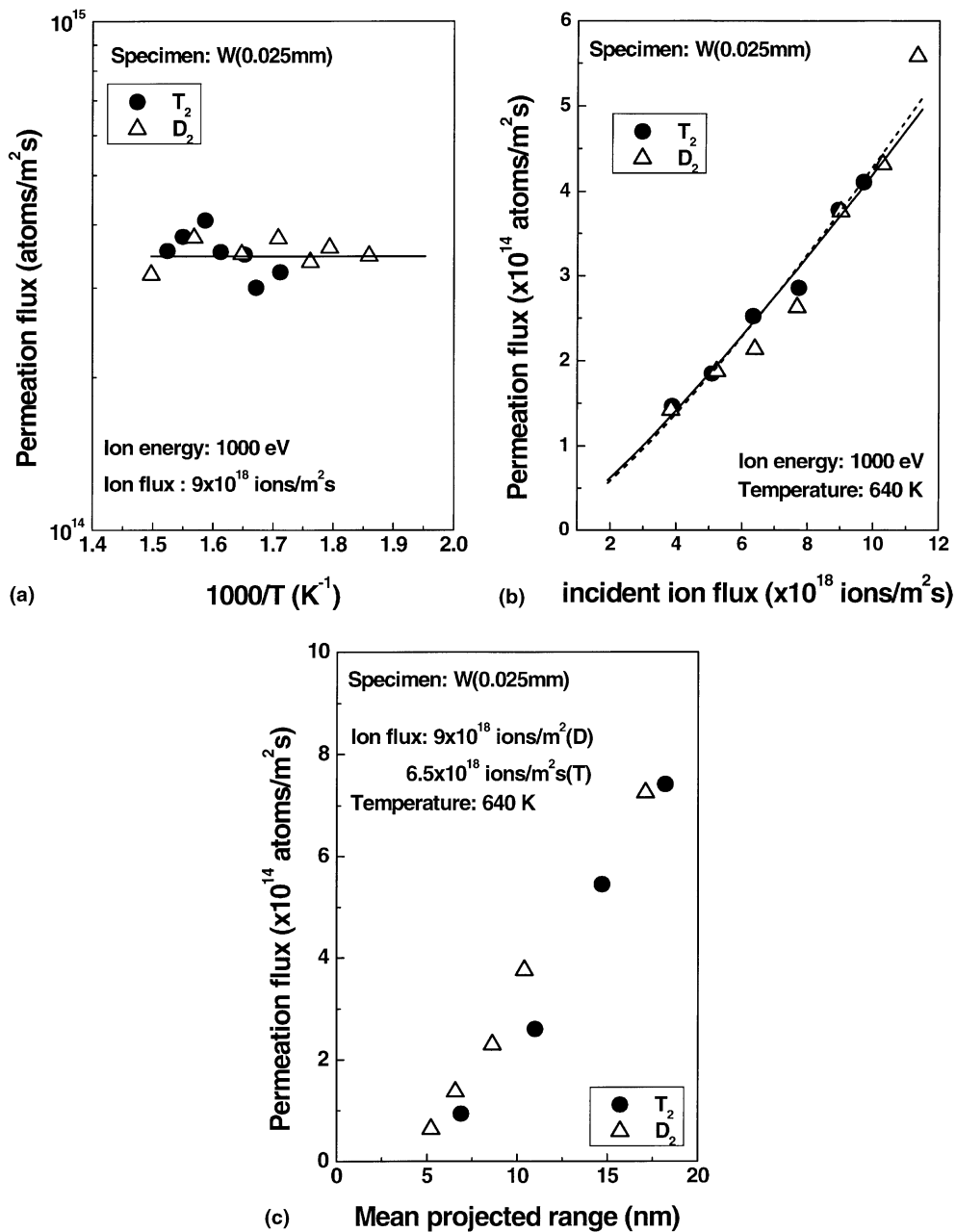


Fig. 3. Parameter dependencies of the permeation of deuterium and tritium through pure tungsten at steady state. (a) Temperature dependence of the permeation fluxes of D and T, (b) incident ion flux dependence of the permeation fluxes of D and T, and (c) incident ion energy dependence of the permeation of D and T, where, incident ion energy was converted to the mean projected range.

implantation side and permeation side as shown in an equation of Table 1. Additionally the isotope effect of the mean projected range predicted by TRIM calculation [15] is small. Therefore, significant isotope effect will not appear on the steady state permeation in DD regime. The present experimental observation does not contradict with the above discussions.

### 3.2. Permeation behavior at transient state

Transient behavior of the permeation of D and T was also analyzed. The 'lag time', which was derived from the difference between the 'beam on' time and the time axis intercept of a 'steepest-slope' line tangent to the permeation signal, was derived for D and T, respec-

Table 1

Clarification of steady-state hydrogen transport model proposed by Doyle and Brice [16,17] with the expressions of permeation flux

Regime	$\phi_p$ Expression	$\phi_i$ Dependence	$r$ Dependence
RR	$\phi_p = \frac{k_b}{k_b + k_f} \alpha \phi_i$	$\phi_p \propto \phi_i$	Independent
DR	$\phi_p = \frac{r^2 k_b}{D_f} (\alpha \phi_i)^2$	$\phi_p \propto \phi_i^2$	$\phi_p \propto r^2$
RD	$\phi_p = \frac{D_b}{d \sqrt{k_f}} \sqrt{\alpha \phi_i}$	$\phi_p \propto \sqrt{\phi_i}$	Independent
DD	$\phi_p = \frac{r D_b}{d D_f} \alpha \phi_i$	$\phi_p \propto \phi_i$	$\phi_p \propto r$

where,  $\phi_p$ : permeation flux,  $\phi_i$ : incident flux,  $D$ : diffusion coefficient,  $k$ : recombination coefficient,  $r$ : range,  $d$ : thickness of foil,  $\alpha$ : sticking coefficient subscripts f: implantation side, b: permeation side.

tively. This lag time, which was proposed by Longhurst [18] theoretically for analysis of the permeation strongly affected by trap effect, should be distinguished from the ‘time-lag’, which is one of the methods to derive the diffusion coefficient.

Fig. 4 shows the temperature dependence of observed lag time for D and T. This figure also shows the reported

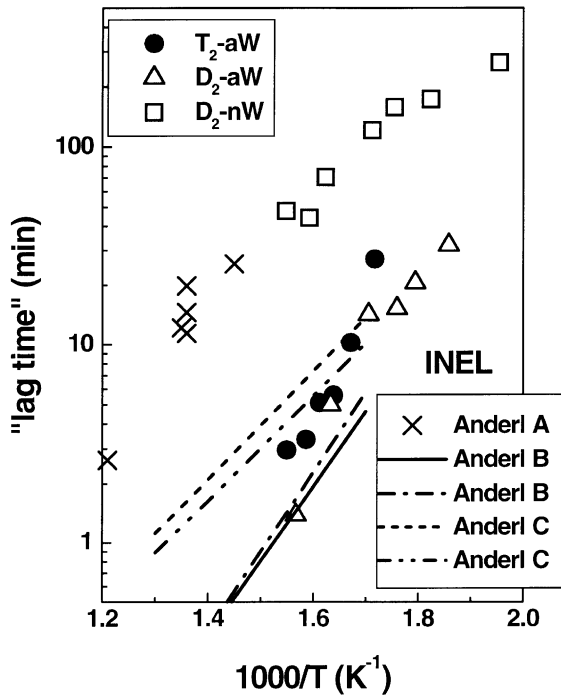


Fig. 4. Temperature dependence of lag time, where, D-aW and T-aW mean results of deuterium and tritium observed in the present experiment, respectively. D-nW means result of deuterium in the unannealed tungsten. A, B, and C mean unannealed tungsten, annealed tungsten at 1627 K and annealed tungsten at 1273 K, respectively, reported by Anderl et al. [7].

lag time of deuterium with several tungsten foils by Anderl et al. [7]. Observed lag time is almost agreed with those by Anderl et al. The difference of lag time between annealed and unannealed tungsten was observed for deuterium, and it has been discussed in the other reports [10,11]. The absolute values of lag times of D and T for the annealed tungsten foil were almost similar. There are, however, slight difference in the temperature dependence as shown in Fig. 4. Observed difference indicates isotope effect on the transient permeation behavior.

In the previous report [11], it was shown that the deuterium permeation implanted into unannealed tungsten foil could be expressed with the assumption of existence of trap site, with the trap energy of 0.9 eV and trap density of 40 ppm according to TMAP [19] analysis. On the other hand, the transient permeation curves of deuterium implanted into annealed tungsten foil could be expressed by the simple diffusion equation with effective diffusion coefficient which involves virtually indistinguishable trap effect from the reduce of the diffusion coefficient. Based on such result, the effective diffusion coefficient of tritium in annealed tungsten was determined in order to discuss the isotope effect on the transient permeation behavior in detail.

When the IDP is controlled by the DD regime, the transient permeation behavior at permeation rising can be expressed by the diffusion equation in Eq. (1) under the initial and boundary conditions in Eqs. (2) and (3),

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} + \phi_i(t) \delta(x-r), \tag{1}$$

$$\phi_i(0) = 0, \phi_i(t) = \phi_i, \tag{2}$$

$$C(0,t) \approx 0, C(d,t) \approx 0, \tag{3}$$

where  $C(x,t)$ ,  $D$ ,  $\phi_i(t)$ ,  $r$  and  $\delta(x-r)$  are hydrogen concentration, diffusion coefficient, incident flux, mean projected range and delta function, respectively.  $C(0,t)$

and  $C(d, t)$  mean hydrogen concentration at implanted surface and permeation surface, respectively.

According to the report by Tanabe et al. [4], the permeation flux can be expressed by Eq. (5) by solving Eqs. (1) ~ (2) under the condition of  $r \ll d$ ,

$$\phi_p(t) = -D \frac{\partial C(d, t)}{\partial x}, \quad (4)$$

$$\frac{\phi_p(t)}{\phi_p(\infty)} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-D \left(\frac{n\pi}{d}\right)^2 t\right), \quad (5)$$

where  $\phi_p(t)$  and  $\phi_p(\infty)$  mean permeation flux at time  $t$  and steady state, respectively. Therefore, Eq. (5) was used to determine the diffusion coefficient from transient permeation analysis.

Fig. 5 shows temperature dependence of derived effective diffusion coefficient of D and T in tungsten. This figure also shows the hydrogen diffusion coefficient in tungsten reported by Frauenfelder [20]. In Fig. 5, the effective diffusion coefficient derived by curve-fitting was quite smaller than that reported by Frauenfelder, and slight difference was observed in effective diffusion coefficient between D and T as well as observed lag time as shown in Fig. 4. Obtained effective diffusion coefficients of D and T derived by least-square fitting in the same temperature range (580–660 K) shown in Fig. 5 are represented in Eqs. (6) and (7), respectively,

$$D_{\text{eff}}^{\text{D}} = 3.60 \times 10^{-9} \exp(-58.7 \text{ kJ/mol}/RT) \text{ (m}^2/\text{s)}, \quad (6)$$

$$D_{\text{eff}}^{\text{T}} = 6.74 \times 10^{-8} \exp(-70.1 \text{ kJ/mol}/RT) \text{ (m}^2/\text{s)}. \quad (7)$$

As to the effective diffusion coefficient ( $D_{\text{eff}}$ ), it is known that the  $D_{\text{eff}}$  is given in Eqs. (8) and (9) with the diffusion coefficient ( $D$ ) and trapping parameter ( $\zeta$ ) [18],

$$D_{\text{eff}} = \zeta D, \quad (8)$$

$$\zeta = \frac{\lambda^2 \nu}{\rho D} \exp\left(-\frac{E_t}{kT}\right), \quad (9)$$

where  $\lambda$  is the material lattice spacing,  $\nu$  is the Debye frequency,  $\rho$  is the trap site density, and  $E_t$  is the trap energy.

Observed small  $D_{\text{eff}}$  could be attributed to the trapping parameter shown in Eq. (9), which is virtually indistinguishable from the reduction of diffusion coefficient as well as that in the previous report [11]. When the diffusion coefficient is known, the trap effect represented trapping parameter in Eq. (9) will be derived. However, since there are uncertainties on the extrapolation of Frauenfelder's diffusion coefficient in a lower temperature range, which has been measured at higher temperature above 1200 K, it is difficult to discuss the trapping effect in the annealed tungsten qualitatively in this position. Further database of trapping effect in the tungsten is desired deeper discussion of trap effect in tungsten.

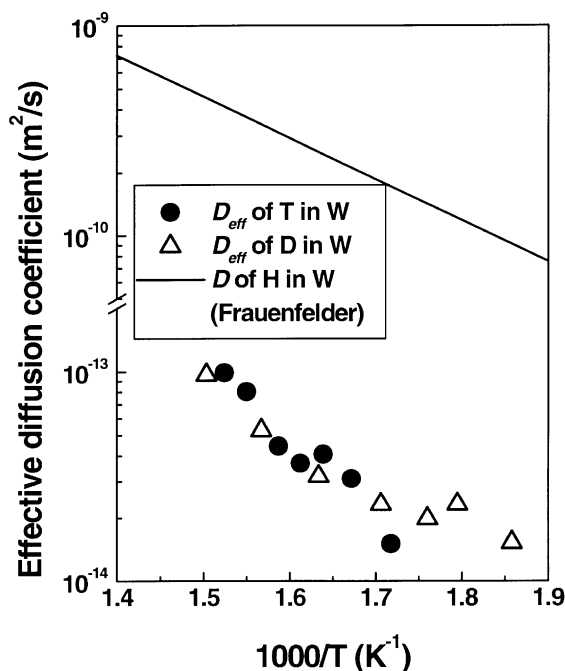


Fig. 5. Temperature dependence of effective diffusion coefficient of deuterium and tritium in pure tungsten annealed at 1273K.

### 3.3. Isotope effect of effective diffusion coefficient

There is slight difference in activation energy of diffusion between D and T in Eqs. (6) and (7). The  $D_{\text{eff}}$  is expressed by the trapping parameter and diffusion coefficient as shown in Eqs. (8) and (9). Generally, it is believed that trapping effect does not include isotope effect, whereas the diffusion process does. Isotope effect of diffusion coefficient is known to be expressed in Eq. (10) [21],

$$D^{\alpha}/D^{\beta} = (m^{\beta}/m^{\alpha})^{1/2}, \quad (10)$$

where  $D^{\alpha}$  and  $D^{\beta}$  are the diffusion coefficients of species of mass  $m^{\alpha}$  and  $m^{\beta}$ , respectively.

According to Eq. (10), the diffusion coefficient should be inversely proportional to the square root of the mass ratio, while the activation energy of diffusion should be independent. However, the obtained activation energies of effective diffusion coefficient between D and T were different. The reported isotope effects are inconsistent with the theoretical prediction. For example, reported isotope effects of the hydrogen diffusion in metal were summarized by Vögle and Alefeld [21], where, for fcc metals, the activation energy of diffusion was reported to decrease with the mass increase, and on the other hand, for bcc metals, the activation energy of diffusion is

reported to increase with the mass in contrast to fcc metals.

There are quite a few reports on hydrogen diffusion in tungsten, which is one of the bcc metals. However, there are no reports on isotope effect of hydrogen diffusion in tungsten. It is difficult to declare, the tendency of observed activation energy of  $D_{\text{eff}}$  in tungsten for D and T, where larger activation energy was observed for larger mass isotope, agreed with that for the bcc metals (Nb, Ta, V [21]) as summarized by Vögle and Alefeld. Because derived  $D_{\text{eff}}$  of D and T in annealed tungsten involves indistinguishable trap effect as mentioned in previous section, the possibility that observed isotope effect on  $D_{\text{eff}}$  can be attributed to isotope effect of the trapping parameter between D and T cannot be neglected.

For further understanding on the tritium transport characteristics in tungsten, it will be desirable to carry out additional experiment on a well-characterized tungsten specimen, such as trap free or trap reduced specimen, in order to exclude the influence of trap effect in tungsten. By knowledge of further experiment, it will be possible to clarify the isotope effect on hydrogen isotope diffusion in tungsten. And it would be useful for more accurate estimation of tritium permeation or retention in a fusion reactor.

#### 4. Conclusion

A first tritium permeation experiment through pure tungsten was successfully carried out using pure tritium ion beam in TPA at JAERI.

The results revealed that at steady-state permeation fluxes of D and T were independent of specimen temperature, were proportional to the ion flux, and increased with the ion energy, indicating that the permeation was controlled by diffusion in both sides (DD regime). The permeation behavior of D and T showed almost the same characteristics. No significant isotope effect was observed on the permeation behavior between deuterium and tritium at steady state. These results were consistent with the theoretical transport model proposed by Doyle and Brice.

On the other hand, isotope effect was observed on the lag time and effective diffusion coefficient obtained through analysis of transient behavior. Obtained effective diffusion coefficient for tritium had a larger activation energy than that for deuterium. Although this result was not consistent with the theoretical description by

classical diffusion theory, it was consistent with the reported isotope effects for bcc metal, to which tungsten belongs.

#### Acknowledgements

Authors would like to thank Drs M. Seki and S. Seki for their continuous encouragement to this work. Authors also would like to acknowledge Dr R. Causey for his helpful discussions on this work.

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