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Permeation behaviour of deuterium implanted into pure aluminium

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Abstract

Implantation driven permeation (IDP) behaviour was investigated for deuterium implanted at low energy (100–1800 eV) into pure aluminium to simulate the behaviour of tritium. The experimental results showed that steady state IDP fluxes Φ_p of deuterium depended on the incident deuterium ion (D^+) fluxes Φ_i according to the relation $\Phi_p = \alpha(\Phi_i)^{1/2}$, under the following conditions: $\Phi_i \approx 7 \times 10^{13} \sim 1 \times 10^{15}$ D^+ cm^{-2} s^{-1}, sample temperature approximately 550 ~ 825 K, and incident D^+ ion energy approximately 300 ~ 1500 eV. This fact suggests that the IDP process through pure aluminium was controlled by recombination of deuterium at the incident surface and by deuterium diffusion at the permeation side. The activation energy for implantation driven permeation of deuterium through pure aluminium was determined to be 59.9 ± 5.0 kJ mol^{-1} under the above experimental conditions.

1. Introduction

Knowledge of implantation driven permeation (IDP) behaviour of hydrogen isotopes, especially tritium, through first wall materials is important for estimating hydrogen isotope recycling and the safety of fusion reactors. Many experiments to study the IDP behaviour of hydrogen isotopes through various materials have been performed with ion beams with energy higher than a few kiloelectronvolts [1–7], or by the discharge method with energy lower than a few 100 eV [8–11]. In design work for FER and ITER, however, IDP data of tritium with energy lower than a few kiloelectronvolts is important to estimate amounts of tritium permeated through first wall materials. A few models for the IDP behaviour have been discussed theoretically [12–15], however, models are insufficient to explain the IDP data for various materials. Therefore, to develop better theoretical models of the IDP behaviour, IDP data to lower monochromatic energies (around 100 eV to a few keV) are required through various materials.

Therefore, we have developed an experimental apparatus to study the IDP behaviour of tritium with variable incident energies ranging from 100 eV to 2 keV using a small ion accelerator [16]. We have already reported IDP data of deuterium through 304 stainless steel [17] and nickel [18] looking at the dependence of deuterium permeation fluxes on incident ion energy, incident ion flux and target temperature. In the present work, IDP of deuterium through pure aluminium was similarly investigated and the rate-determining process for IDP behaviour is also discussed.

2. Experimental details

2.1. Apparatus

The experimental apparatus developed for IDP experiments consists of the following five main systems: (1) an ion source for production of a hydrogen isotope ion beam with high flux and variable low energies, (2) a main chamber system for ion implantation, (3) a system for measurement of the gases permeated through the target, (4) a hydrogen isotope gas supply and recovery system, and (5) a vacuum pump system. The apparatus has been installed in a glovebox in the Tritium Process Laboratory (TPL) at the Japan Atomic Energy Research Institute (JAERI). More details of the apparatus are described in a previous paper [16].

The ion source was a modified quartz capillary duoPIGatron by Isoya and Inoue [19]. More than 90% of the ion species in the extracted beams was found to be the D^+ ion by analysis with a mass spectrometer. The other species were D_2^+ and D_3^+. The D^+ ion energy could be varied from 100 eV to 2 keV and the maximum ion fluxes on the target ranged from 1×10^{14} D^+ cm^{-2} s^{-1} at 100 eV to 1×10^{15} D^+ cm^{-2} s^{-1} at 2 keV. The effective implantation area of the target is the central region 25 mm in diameter.

2.2. Sample and procedure

Pure aluminium (99.999%) metal samples from Japan Lamp Industries were cut into discs 34 mm in diameter from a foil of 0.1 mm thickness, for use as the target for IDP experiments. These discs were polished mechanically with emery paper before use.

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The sample disc and a thermocouple were clamped on the target flange, fixed in the main chamber, and heated to about 850 K for more than 3 h under vacuum to degas, using a halogen lamp installed just behind the target on the permeation side. After degassing of the sample, D^+ ions with an energy of 2 keV and a flux of 1×10^{15} D^+ cm^{-2} s^{-1} were implanted into the target at 825 K for about 6 h to prepare the incident sample surface prior to a series of IDP experiments. Furthermore, 2 keV D^+ implantation at a flux of 1×10^{15} D^+ cm^{-2} s^{-1} was carried out for the first hour every day. After this pre-implantation treatment, permeation fluxes through target samples reached steady-state values and were completely repeatable. These sample surfaces were analysed by off-line Auger electron spectrometry after implantation, however, no impurity peaks were observed except those caused by oxygen.

After the above sample treatment, the following series of implantation experiments was performed. For the experiments to determine the dependence of the permeated fluxes on the incident flux, D^+ fluxes of about 7×10^{13} to 1×10^{15} D^+ cm^{-2} s^{-1} were implanted in the target at each temperature (550 and 825 K) and incident ion energy (300, 700 and 1500 eV). For other experiments, the incident D^+ ion flux was always controlled to 2.5×10^{14} D^+ cm^{-2} s^{-1}. The experiments on the dependence of permeated fluxes on the target temperature were performed at temperatures ranging from 550 K to 825 K for each incident ion energy (300, 500, 700, 1000 and 1500 eV). The dependence on incident ion energy was measured at energies ranging from 100 eV to 1800 eV, and at two temperatures (550 and 825 K).

The permeated fluxes were measured by a quadrupole mass spectrometer ($m/e=3$ and 4), calibrated by the capillary method. IDP fluxes were determined from the difference of the above mass peaks during implantation and with the beam shut out. During these experiments, the pressure of the upstream (incident) side in the main chamber was controlled at 4×10^{-4} Pa by a cryopump, though the base pressure was below 3×10^{-6} Pa. The base pressure of the downstream (permeation) side was kept below 1×10^{-6} Pa by an ion-sputter-pump. This downstream base pressure rose to 3×10^{-5} Pa with increasing target temperature.

3. Results and discussion

3.1. Incident ion energy dependence

To investigate the effect of incident ion energy on the permeation fluxes, IDP experiments were performed under the following conditions: (1) incident ion energy of about 100 ~ 1800 eV, (2) incident ion flux constant at 2.5×10^{14} D^+ cm^{-2} s^{-1}, (3) target temperature of 550 and 825 K. During D^+ implantation, an increase in the target temperature of about 5 K was always observed, however, this increase was almost constant during implantation of D^+ of various energies. The results are summarized in Fig. 1, showing the relationship between incident ion energy and permeation flux at steady state. There was no clear energy dependence for the permeation flux observed for 304 SS in the previous study [17], *i.e.* the permeation fluxes were almost constant for the incident energies (given above) at 825 K. Moreover, a small increase in permeation fluxes was observed with increasing incident ion energy at 550 K, though the permeation fluxes clearly decreased with increasing incident ion energy for 304 SS. One of the possible reasons for this tendency might be drawn from the report by Den and Robinson [20]. In their theoretical calculation of hydrogen implanted into aluminium, the particle reflection fraction could be expected to decrease with an increase in energy reduction at the incident surface. The amount of energy reduction of the implanted particles would be in proportion to the incident energy at the same incident angle against the surface. Therefore, the probability that the incident ion would pass through the surface, and not reflect, would increase with incident energy under the above energy conditions. If this theoretical calculation is applicable, the above tendency of the permeation flux to increase with incident ion energy would be reasonable.

3.2. Incident ion flux dependence

As mentioned above, experiments for incident ion flux dependence were performed under the following conditions: (1) incident ion flux of around 7×10^{13} to 1×10^{15} D^+ cm^{-2} s^{-1}, (2) incident ion energy of 300, 700, and 1500 eV, (3) target temperature of 550 and 825 K. As shown in Fig. 2, the permeation fluxes Φ_p

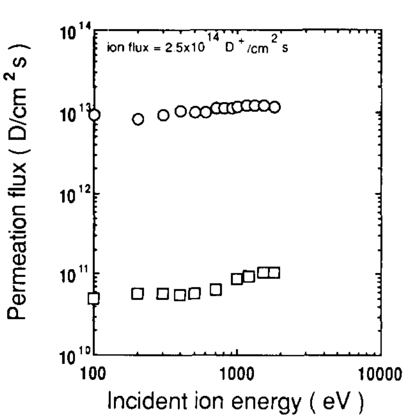

Fig. 1. Incident ion energy dependence of IDP fluxes for deuterium implanted into pure aluminium at a constant incident ion flux of 2.5×10^{14} D^+ cm^{-2} s^{-1} at target temperatures of 550 K (□) and 825 K (○).

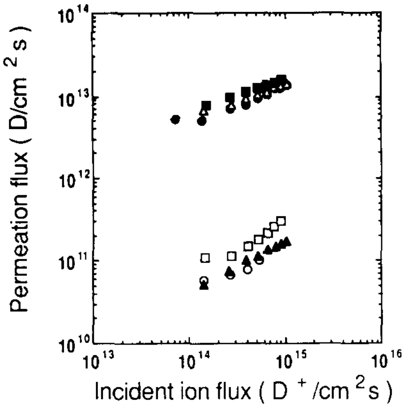

Fig. 2. Incident ion flux dependence of the IDP flux for deuterium implanted into pure aluminium at various ion energies and temperatures: 300 eV, 550 K (○); 700 eV, 550 K (▲); 1500 eV, 550 K (□); 300 eV, 825 K (●); 700 eV, 825 K (△); 1500 eV, 825 K (■).

TABLE 1. Values of n in eqn. (1), $\Phi_p = \alpha(\Phi_i)^n$, determined from Fig. 2

Energy (eV)	Sample A		Sample B	
	825 K	550 K	825 K	550 K
300	0.50	0.32	0.29	0.53
700	0.46	0.60	0.31	–
1500	0.40	0.58	0.46	0.74
Mean value	0.48 ±	0.10	0.46 ±	0.16

Samples A and B had surfaces polished by emery paper.

depend significantly upon the incident ion fluxes Φ_i according to the relationship:

$$\Phi_p = \alpha(\Phi_i)^n \tag{1}$$

where α is an arbitrary constant.

In Table 1, the values of n determined in the above equation are summarized for each set of experimental conditions. The mean value of n was found to be 0.47 ± 0.13.

From a steady state model given by Doyle and Brice [13, 15] and Kerst and Swansiger [8], the IDP process of hydrogen isotopes implanted into metals can be divided into three or four categories depending on whether the rate-determining step is the recombination reaction (R) or diffusion process (D) for hydrogen isotopes, at the front or back side of the metal. That is, the categories depend on (1) the recombination reaction at both surfaces (RR regime), (2) recombination at the front surface and diffusion at the back side (RD regime), (3) diffusion at both sides (DD regime), and (4) diffusion at the front side and recombination at the back surface (DR regime). The value of n in eqn. (1) is important for identifying to which regime the observed IDP process corresponds.

From application of the above model, values of n are expected to be unity for RR and DD regimes, 0.5 for the RD regime, and are not expected to be constant for the DR regime.

The results of this work, in which the value of n determined was 0.47, would suggest that the observed IDP process of deuterium through pure aluminium is controlled by the RD regime under the above experimental conditions. The results of this work also corresponded to the prediction by Doyle [13]. However, Tanabe *et al.* [4] explained his IDP data for 30 keV D^+ ions with 1×10^{15} D^+ cm^{-2} s^{-1} through aluminium using the DD regime. This difference between the present work and the report of Tanabe *et al.* [4] might be caused by the difference in incident energy.

3.3. Target temperature dependence

If the IDP process corresponds to the RD regime, as discussed above, the permeation fluxes could be expressed by the following equation and would depend on the target temperature because of the temperature dependence of the diffusion coefficient D and recombination coefficient K_r:

$$\Phi_p = \beta(D/d)(\Phi_i/K_r)^{1/2} \tag{2}$$

where d is the sample thickness and β is an arbitrary constant.

In Fig. 3 the results of the temperature dependence for permeation fluxes under the following conditions are summarized: (1) incident ion energy of 300, 500, 700, 1000, and 1500 eV, (2) incident ion flux constant at 2.5×10^{14} D^+ cm^{-2} s^{-1}, (3) target temperature of approximately 550 ~ 825 K. In this figure, the permeation fluxes are plotted against the reciprocal target temperature at each incident energy. From this Arrhenius plot, the permeability of deuterium implanted into pure

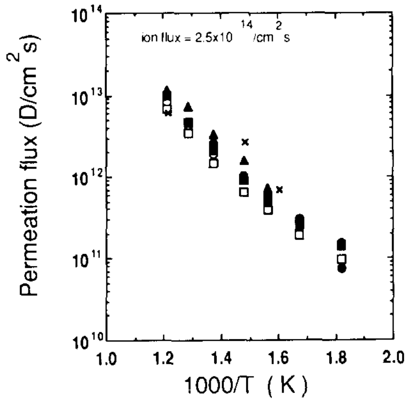

Fig. 3. Arrhenius plot of the permeation flux of deuterium implanted into pure aluminium at a constant incident ion flux of 2.5×10^{14} D^+ cm^{-2} s^{-1}, at various ion energies: 300 eV (●), 500 eV (○), 700 eV (▲), 1000 eV (□), 1500 eV (■). The symbols × are the data reported by Tanabe *et al.* [5].

aluminium was found to be clearly dependent on the target temperature and to be almost the same at each incident energy, as expected from the results of Figs. 1 and 2. The permeation fluxes through pure aluminium at 825 K were about 3 ~ 20 times larger than that found for 304 SS in this region of incident ion energy in the previous study [17], though they were almost the same at 550 K. The data reported by Tanabe *et al.* [5] are also shown in this figure. These data almost correspond, considering the difference in incident ion flux and energy. The activation energy E_p of the permeation process for deuterium implanted into pure aluminium was determined at each incident ion energy from Fig. 3 and is given in Table 2. These values are almost the same and the mean value was 59.9 ± 5.0 kJ mol^{-1}.

From the model of Baskes [12], Doyle [13], Kerst and Swansiger [8] and Brice and Doyle [15], E_p could be expressed as follows, assuming the observed IDP process corresponds to the RD regime:

$$E_p = (E_d + E_s)/2 \tag{3}$$

where E_d and E_s are the activation energies for diffusion and solution respectively. If the values of E_d (45.6 kJ mol^{-1}) and E_s (58.2 kJ mol^{-1}) for hydrogen reported by Eichenauer *et al.* [21, 22] were used, then a value of E_p of 51.9 kJ mol^{-1} would be expected from eqn. (3). This expected value almost corresponds with the above determined value within experimental error.

3.4. Recombination factor

In eqn. (2), D and K_r are expressed as $D = D_0 \exp(-E_d/RT)$ and $K_r = K_{r0} \exp(-E_{Kr}/RT)$ respectively. So, eqn. (2) can be expressed as

$$\Phi_p = \beta(D_0/d)(\Phi_i/K_{r0})^{1/2} \exp\{-(E_d - E_{Kr}/2)/RT\} \tag{4}$$

where D_0 and K_{r0} are pre-exponential factors of diffusivity and recombination reactivity respectively, and E_{Kr} is the activation energy for the recombination reaction.

So, from eqn. (4), E_p and E_{Kr} are expressed as

$$E_p = E_d - E_{Kr}/2 \tag{5}$$

TABLE 2. Activation energies E_p (kJ mol^{-1}) for the permeation process of deuterium implanted into pure aluminium determined from fig. 3

Incident ion energy (eV)	Activation energy (kJ mol^{-1})
300	67.1
500	53.4
700	62.3
1000	58.0
1500	58.5
Mean value	59.9 ± 5.0

$$E_{Kr} = 2(E_d - E_p) \tag{6}$$

As E_d was reported as 45.6 kJ mol^{-1} by Eichenauer and Pebler [21], we can calculate E_{Kr} to be -28.6 kJ mol^{-1} from eqn. (6). K_r also could be determined from each IDP data set, using reported data for D [21] and eqn. (2) if β is constant. In Fig. 4, the determined value of K_r is plotted against the reciprocal target temperature, assuming $\beta = 1$ in eqn. (4). Though the determined K_r value fluctuated a little, the mean value of E_{Kr} from the above data at each incident energy was -29 ± 9 kJ mol^{-1}, and of course equal to -28.6 kJ mol^{-1} from eqn. (6). The values of K_r are almost the same order as those from Baskes [12] (as also shown in Fig. 4). However, the K_r values of hydrogen on aluminium reported by Kamada *et al.*, using the elastic recoil detection method below 500 K [23], were several orders of magnitude smaller than the present values even if the value of D is used from the same reported equation.

From the model of Baskes [12], E_{Kr} could be expressed as,

$$E_{Kr} = E_x - 2E_s \tag{7}$$

where E_x is the activation energy for entering the bulk and expressed as $E_x = E_d + E_s > 0$ for endothermic metal, $E_x = 0$ for exothermic metal. As aluminium is an endothermic metal, E_{Kr} could be expected to be -12.6 kJ mol^{-1} from eqn. (7) if the reported values of E_d and E_s [21, 22] are used. Although this expected value is about half that determined above, they are the same "minus" activation energy for the recombination reaction. This difference would be caused by the difference

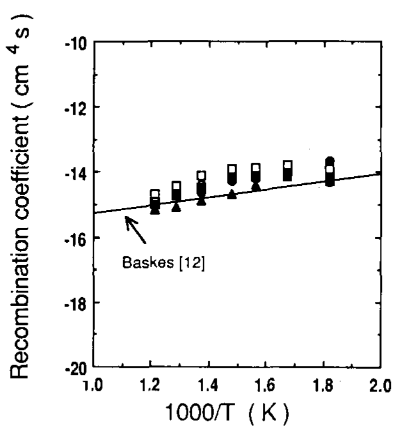

Fig. 4. Arrhenius plot of the recombination coefficient at the front surface for deuterium implanted into pure aluminium determined from the IDP data using eqn. (3), at various ion energies: 300 eV (●), 500 eV (○), 700 eV (▲), 1000 eV (□), 1500 eV (■). The solid line shows the calculated value for aluminium reported by Baskes [12].

in the surface states through which the deuterium entered the aluminium bulk in the experiments to determine E_d and E_s [21, 22] and in the work reported here.

In contrast, from the model of Pick and Sonnenberg [14], E_{Kr} can be expressed as

$$E_{Kr}=2(E_c-E_s) \tag{8}$$

where $2E_c$ is the activation energy of the sticking probability that a hydrogen molecule impinging on the surface will dissociate and that the resulting hydrogen atoms will stick to the surface at a chemisorption site. E_c is zero when the surface is sufficiently clean. If we adopt this model for the observed IDP data, the surface would not be clean and $2E_c$ could be calculated to be approximately 0.9 eV (88 kJ mol^{-1}). This value of $2E_c$ for aluminium seems to be large compared with that of copper (approximately 0.2 eV) [24]. However, that of nickel was reported to be 0.87 eV [25], and ours might be reasonable if one considers the effect of the surface oxygen barrier.

In both models, a kind of activation barrier existed for deuterium entering the aluminium bulk. This activation barrier was expected to be E_d+E_s (1.1 eV) according to the Baskes model [12] and was almost equal to 0.9 eV according to the model of Pick and Sonnenberg [14].

4. Conclusion

The implantation driven permeation (IDP) behaviour of deuterium through pure aluminium was investigated under the following experimental conditions: (1) incident ion (D^+) energy of around 100 ~ 1800 eV, (2) incident ion flux of about $7\times10^{13}\sim1\times10^{15}$ D^+ cm^{-2} s^{-1}, and (3) target temperature of 550 ~ 825 K. The experimental results showed that the steady state IDP fluxes Φ_p for deuterium depended on the incident deuterium ion (D^+) fluxes Φ_i according to the relationship $\Phi_p=\alpha(\Phi_i)^{1/2}$. This would suggest that the IDP process of deuterium through pure aluminium was controlled by recombination of deuterium at the incident surface and by deuterium diffusion at the permeation side (RD regime). The activation energy for the permeation of deuterium implanted into pure aluminium was determined to be 59.9 ± 5.0 kJ mol^{-1} under the above experimental conditions. The activation energy for the recombination of deuterium implanted into pure aluminium was also determined to be -29 ± 9 kJ mol^{-1}, assuming the RD regime. In general, all series of observed IDP data through pure aluminium could be understood by the Baskes model [12] rather than by the Pick and Sonnenberg model [14].

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