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**Basic Study on Permeation and Inventory
of Hydrogen Isotopes in Plasma-Facing Metals**

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Chapter 1 Introduction

In the D-T burning experiments of the JET tokamak [1], a large amount of tritium was retained in the torus, which reminded one the importance of hydrogen recycling between the plasma and the plasma-facing walls on the safety of D-T fusion reactors. As tritium is a radioisotope and scarcely exists in nature, its effective confinement in the reactor system is the major issue regarding the fuel economy as well as the reactor safety. Therefore, it is needed to study on hydrogen recycling and related basic processes.

The plasma-wall interaction (PWI) [2] concerned with the hydrogen recycling, schematically shown in Fig.1.1, contains many processes such as diffusion and trapping in the walls, and reflection, desorption, reemission and permeation from the walls. Among them, the desorption induced by ions and electrons and the reflection are non-thermally activated processes which are independent of the wall temperature. Both of them have been well known as Wilson [2] reviewed.

When metals such as stainless steels, nickel and iron are exposed to hydrogen plasmas, a large amount of hydrogen permeates through the metals, which is known as the plasma-driven permeation (PDP). The PDP would directly cause a significant leakage of tritium to the environment system. It would also increase an tritium inventory, which is the amount of tritium retained in the plasma-facing walls, since the large permeation flux means the high concentration of tritium in the walls. Fast neutrons and alpha particles produce radiation damages in the plasma-facing walls, in which hydrogen isotopes would be trapped. Hence also the traps would increase the tritium inventory.

Therefore, thermal behaviors of hydrogen isotopes such as diffusion, permeation and trapping are directly related with the tritium leakage and inventory in the walls. In the present work, experimental studies on the thermal behaviors of hydrogen in metals exposed to hydrogen plasmas were performed.

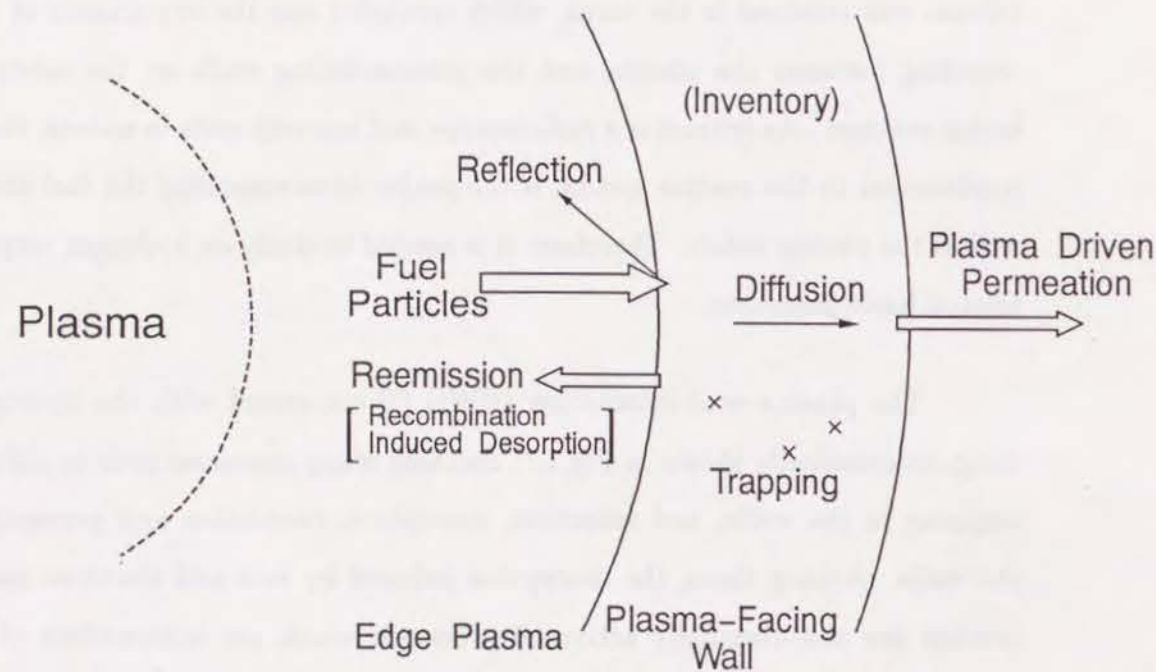


Fig. 1.1. An illustration of plasma-wall interaction processes responsible for fuel particle recycling.

In the followings of this chapter, studies on the hydrogen permeation, the plasma-driven permeation (PDP) and the hydrogen trapping will be reviewed and the objectives of the present work will be described.

1.1 Hydrogen permeation in metals

It has been well known for more than a hundred years that hydrogen permeates through metals when the metals are exposed to hydrogen gas (GDP – gas driven permeation) [3–5]. The fact that hydrogen diffuses as an atom, not a molecule, in metals to permeate was suggested at the end of the nineteenth century [6]. At the beginning of the twentieth century, the Richardson's equation [7], which gave the steady-state permeation flux J_{st} , was proposed. It is expressed as

$$J_{st} = \frac{a}{L} P^{1/2} \exp(-b/T) \quad , \quad (1.1)$$

where L and T are the thickness and the temperature of the metal membrane, respectively, P the hydrogen gas pressure, and the parameters a and b constants. This equation is used for the case where one side of the membrane is exposed to hydrogen gas and the other side to vacuum. When the other side is exposed to hydrogen gas of the pressure P_d , $P^{1/2}$ in the right side of Eq.(1.1) should be replaced by $(P^{1/2} - P_d^{1/2})$. Using the Richardson's equation, many experimental studies on hydrogen permeation in various metals have been performed [8–13].

It was found that the equilibrium concentration of hydrogen dissolved in metals was proportional to the square root of the ambient hydrogen gas pressure in 1911 [8], which is now known as Sieverts' law. It is written by

$$C = K P^{1/2} \quad , \quad (1.2)$$

where C is the dissolved hydrogen concentration and K is the solubility of hydrogen in the metal. This equation could explain the pressure dependence of Eq.(1.1) since the dissolved hydrogen diffuses to permeate through metals [14].

Now the Richardson's equation is rewritten by [15]

$$J_{st} = \Phi \frac{P^{1/2}}{L} \quad , \quad (1.3)$$

where Φ is called as the permeation coefficient and defined by

$$\Phi = DK \quad , \quad (1.4)$$

where D and K are the diffusion coefficient and the solubility of hydrogen, respectively. As the temperature dependence of both D and K is expressed by Arrhenius' equation [16], Eq.(1.1) is equivalent to Eq.(1.3).

The diffusion coefficients of hydrogen in metals have been determined in various ways. These are the time-lag method [17–19] that uses the time-dependent changes of the permeation flux, the evolution method [15, 20–23] based on the desorption rate of hydrogen from metals, the weight gain method [24] for metals which form hydrides, the profiling method [25] by a qualitative analysis of hydrogen concentrations in small pieces which are vertically sliced from rods, and others. As the permeation coefficient Φ is obtained from the steady-state permeation flux, the solubility K is given by Eq.(1.4) when the diffusion coefficient D is already known.

Many experiments concerned with the hydrogen permeation, diffusion and solution have been done and some significant results were obtained as listed below.

Isotope effect The isotope effect on the permeation was studied [26] just after deuterium had been found [27]. The diffusion coefficient of tritium was also measured [28]. As the results, the diffusion coefficient and the solubility of each hydrogen isotope were found to differ from each other by no more than the square root of the isotope mass ratio [24, 29–32].

Lattice diffusion Smithells and Ransley [14] showed by permeation experiments of hydrogen in single crystalline iron that hydrogen generally diffused in lattice and not in grain boundaries. In recent years, the lattice and the interstitial sites occupied by hydrogens have been measured by the ion channeling technique [33–37].

Oxide layer It has been known for many years that oxides on the surface of the

metals can act as a barrier against hydrogen permeation [38]. The diffusion coefficients in the oxides were found to be several orders of magnitude smaller than that in the bulk metals [39, 40]. The recent work [41] indicated that surface impurities other than oxygen also decrease the permeation flux.

Square-root law The steady-state permeation flux has not been always proportional to the square root of the hydrogen gas pressure [14, 42]. The square-root law was found to be incorrect when the rate of diffusion was faster than that of hydrogen solution from the gas phase into the bulk metals [43].

The basic information concerned with the GDP (gas-driven permeation) of hydrogen in metals has been obtained as mentioned above.

1.2 Plasma driven permeation

In recent years, Kerst et al. [44, 45] observed a very high permeation flux of deuterium through a stainless steel membrane when it was faced to a deuterium plasma with a magnetic confinement system. It was called as the PDP (plasma driven permeation). The authors observed the deuterium PDP using a small plasma device with a glass discharge tube [46] just after the Kerst's experiments. The permeation flux in the PDP was one thousand greater than that in the GDP under the same gas pressure, which indicated that the PDP could have a large effect on the tritium inventory and leakage in the plasma-facing walls of fusion reactors. The authors also showed by observing the PDP in Heliotron E, one of the largest plasma experimental devices, that the permeation of the PDP depended on the particle recycling of both hydrogen and impurities [47].

The PDP is sometimes distinguished from the ADP (atom driven permeation) and IDP (ion driven permeation) by the characteristics of the incident hydrogen particles.

ADP It has been known for many years that hydrogen molecules were dissociated into atoms by contact with a high temperature tungsten filament [48–50] and the dissociated atoms could be easily absorbed to solids [51]. Livshits et al. [52–54] first observed that the dissociated hydrogen atoms highly permeated through palladium and nickel membranes and named this permeation as the superpermeation. Waelbroeck et al. [43, 55] also observed a similar phenomenon.

IDP Perkins and Noda [56] observed a deuterium permeation through stainless steels which was implanted by a few keV deuterium ions. This IDP has been widely experimentally studied by Tanabe et al. [57, 58], Holland et al. [59–61] and others.

As energetic particles of hydrogen from plasmas consists of neutral atoms and ions, the PDP includes the ADP and the IDP. In the case of rf and low-temperature plasmas of plasma devices, the PDP can be regarded as the ADP since hydrogen particles with low energies are not implanted. In the case of heated plasmas of the plasma devices, where high energy particles from the plasma as well as low energy Franck-Condon atoms would impinge to the surface, both the ADP and the IDP would contribute to the permeation. In the followings, the word “PDP” will be used for the case of the rf and low-temperature plasmas, and distinguished from the permeation caused by high energy ions that penetrate deep in metals.

The processes of the GDP of hydrogen in metals [62] consists of

1. absorption of hydrogen molecules on one surface and subsequent dissociation into atoms,
2. diffusion of atoms in the bulk,
3. recombination of two atoms to a molecule on the other surface and subsequent desorption into the gas phase.

The process **3** is a reverse of the process **1**. Most of the hydrogen molecules in the gas phase incident on the metal surfaces are not dissociated since the surfaces generally have potentials against the dissociation process of **1**. This is the reason why the permeation flux of the GDP is quite small as compared to the incident flux of the molecules.

In the case of the PDP [63–65], it is not needed to be dissociated for atoms. Energetic molecules would be easily dissociated on the surface since the dissociation energy of a hydrogen molecule into atoms is 2.45 eV. This is the reason of a high permeation flux of the PDP. The same reason can be applicable to the IDP [66–68] since high energy particles would directly penetrate deep into the bulk. In the sense of skipping the dissociation process **1**, the IDP is the same as the PDP. The difference between the IDP and the PDP lies on the penetrating depth.

From the above discussions, the diffusion and the recombination processes are mainly responsible for the permeation of the PDP and the IDP. In the process **3** of two atoms recombining to one molecule, the rate of the recombination would be proportional to the square of the hydrogen concentration near the surface. The proportionality constant is called as the recombination coefficient.

Values of the recombination coefficient on nickel, which were experimentally determined by several researchers, differ from each other by several orders of magnitude [69]. The reason would be that the surface impurities such as oxygen impede the adsorption and the desorption processes [70–73]. The recombination coefficient is not a bulk property and depends on the conditions to which the surface is faced. Therefore, it is desirable to measure the recombination coefficient in the large plasma devices whose plasma conditions would be closer to the fusion reactors.

The diffusion coefficient can be obtained by various ways as described in 1.1 and its values in nickel, for example, are well known. For the metals such as iron

which are easily oxidized, however, the values of the diffusion coefficient experimentally obtained are quite different from each other [43, 74, 75]. This is because the methods so far used to determine the diffusion coefficient are affected by the surface conditions. Hence, a new measuring method is needed which is not affected by surface properties. One possible method is to observe the hydrogen concentration in the bulk directly as well as the permeation flux.

There are two ion-beam techniques for observing the concentrations of hydrogen isotopes in solids. One is the elastic recoil detection analysis (ERD) [76] and the another is the nuclear reaction analysis (NRA) using the nuclear reaction $D(^3\text{He}, p)^4\text{He}$ [77, 78]. As compared with the ERD [79, 80], the NRA [81, 82] have some advantages although both hydrogen and deuterium can be observed by the ERD. The probing depth is larger for the NRA while the depth resolution is almost the same with a probing beam of a few-MeV helium. The identification of detected particles is easier for the NRA since energy spectra of the scattered particles and the products of proton and helium are not overlapped.

Combining the PDP measurement for rf plasmas of deuterium and the NRA technique, the permeation flux through a nickel membrane and the deuterium concentration near the surface of the membrane were observed at the same time in the present work. As the result, the parameters of the diffusion coefficient and the recombination coefficient were determined. This measurement provided a new method for determining the diffusion coefficient which was scarcely influenced by the surface impurities as shown later.

1.3 Trapping

As the plasma-facing walls are bombarded by fast neutrons and alpha particles, radiation damages are produced. The damages have deeper potentials for

hydrogen than the solution sites and would trap hydrogen isotopes. So the traps would increase the tritium inventory in the plasma-facing walls. There are no general theories concerned with the traps. Experimental data are required to develop the theory. It is useful to measure concentrations of trapped hydrogen in solids which are bombarded by fast particles and to relate the concentrations with such parameters as the bombardment doses and the damage rates.

There have been two ways to study the hydrogen trapping experimentally. One is the thermal desorption spectroscopy (TDS) [83-90], in which desorption rates of hydrogen from heated samples are measured. By analyzing the desorption spectrum with diffusion equations, activation energies for detrapping and concentrations of the traps are determined. Depth profiles of the traps can not be obtained by the TDS.

The another method is the NRA which is described in the previous section. As the NRA provides depth profiles of deuterium, it has been used for the study on the trapping by many researchers [34, 84, 91-96]. For example, Bohdansky et al. [84] observed the depth profiles of deuterium retained in stainless steels which were implanted by deuterium ions. They showed that two kinds of trapping sites were produced. Besenbacher et al. [93] determined an activation energy for detrapping from the trap which was considered to be associated with helium bubbles in nickel.

It is difficult to distinguish between the trapped and the dissolved deuterium by the NRA. When a sample containing deuterium is kept at high temperatures, the observed deuterium by the NRA may be regarded as trapped ones. In such a case, however, the trapped deuterium is not in equilibrium with the dissolved one. In the fusion reactors, temperatures of the plasma-facing walls are several hundred degrees of the centigrade and steady-state operations of the plasmas are planning [97]. Therefore, it is important to observe the trapped deuterium in the samples which are continuously charged by deuterium at elevated temperatures.

In the present work, the in-situ observations of deuterium by combining the NRA and the PDP measurement were performed for experimental studies on the hydrogen trapping. This method has advantages as the followings:

1. As the sample is continuously charged with deuterium by the rf plasma, there is an equilibrium between the dissolved and trapped hydrogens even at elevated temperatures.
2. The dissolved concentration of deuterium is determined from the permeation flux of the PDP.
3. Knowing the dissolved concentration, the concentration of the trapped deuterium is obtained by subtracting the dissolved one from the observed one by the NRA.

Chapter 2

Equations for hydrogen diffusion and trapping

In this chapter, basic equations concerned with the thermal behaviors of hydrogen in metals such as diffusion, permeation and trapping are described. The diffusion equations and the permeation model have been already known. A new model of the trapping process will be derived here. This covers all models so far proposed as will be shown later.

2.1 Diffusion equations

One dimensional diffusion of hydrogen in a metal membrane with a thickness of L is considered. There is no gradient of the temperature in the membrane. When there are no traps, the diffusion equation is well known as

$$\frac{\partial C_s(x, t)}{\partial t} = D \frac{\partial^2 C_s(x, t)}{\partial x^2} \quad , \quad (2.1)$$

where $C_s(x, t)$ is the concentration of hydrogen dissolved in the metal at a time t and a distance x from the upstream surface. The parameter D is the diffusion coefficient of hydrogen as mentioned in the chapter 1. The diffusion coefficient is assumed to be independent of the hydrogen concentration. The permeation flux $J(t)$ given by Fick's law is expressed as

$$J(t) = -D \left(\frac{\partial C_s(x, t)}{\partial x} \right)_{x=L} \quad . \quad (2.2)$$

When the upstream surface of the membrane is exposed to hydrogen molecular gas (i. e. GDP) or hydrogen plasmas (i. e. PDP) and the opposite downstream surface is faced to vacuum, the boundary conditions of both the surfaces are written

by [63]

$$F = k_u C_s^2(0, t) - D(\partial C_s / \partial x)_{x=0} \quad , \quad (2.3)$$

$$0 = k_d C_s^2(L, t) + D(\partial C_s / \partial x)_{x=L} \quad , \quad (2.4)$$

respectively. Here, k_u and k_d are the recombination coefficients on the upstream and the downstream sides, respectively. The parameter F is an incident flux of hydrogen which impinges on the upstream surface and dissolves near the surface region. In both Eqs.(2.3) and (2.4), the left sides represent the incident fluxes, the first and the second terms of the right sides the reemission fluxes from the surfaces and the diffusive fluxes to the bulk regions, respectively. These boundary conditions are derived from the particle balance of hydrogen.

At the steady-state permeation, Eqs.(2.1) to (2.4) are written as

$$C_s(x) = C_{su} + (C_{sd} - C_{su})x/L \quad , \quad (2.5)$$

$$J_{st} = D(C_{su} - C_{sd})/L \quad , \quad (2.6)$$

$$F = k_u C_{su}^2 + k_d C_{sd}^2 \quad , \quad (2.7)$$

$$J_{st} = k_d C_{sd}^2 \quad . \quad (2.8)$$

Here, J_{st} is the permeation flux and C_{su} and C_{sd} are the hydrogen concentrations near the upstream and the downstream surfaces, respectively. Combining Eq.(2.7) and Eq.(2.8), it can be written that

$$F = R_{st} + J_{st} \quad , \quad (2.9)$$

where R_{st} is the reemission flux at the steady state. It is expressed as

$$R_{st} = k_u C_{su}^2 \quad . \quad (2.10)$$

The boundary conditions and the particle balances at the steady state described above are schematically shown in Fig.2.1(a).

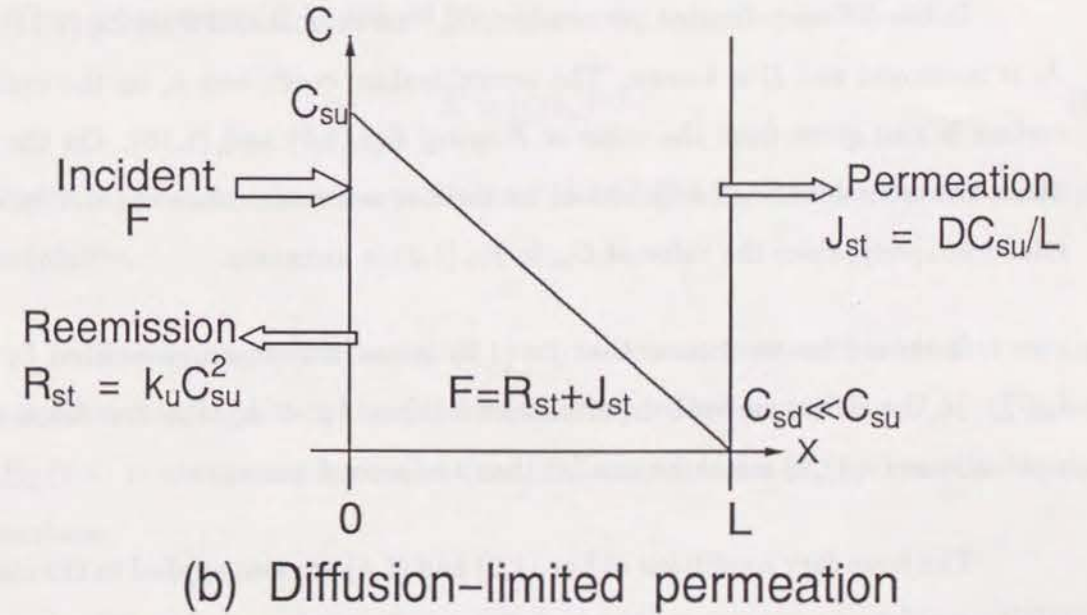
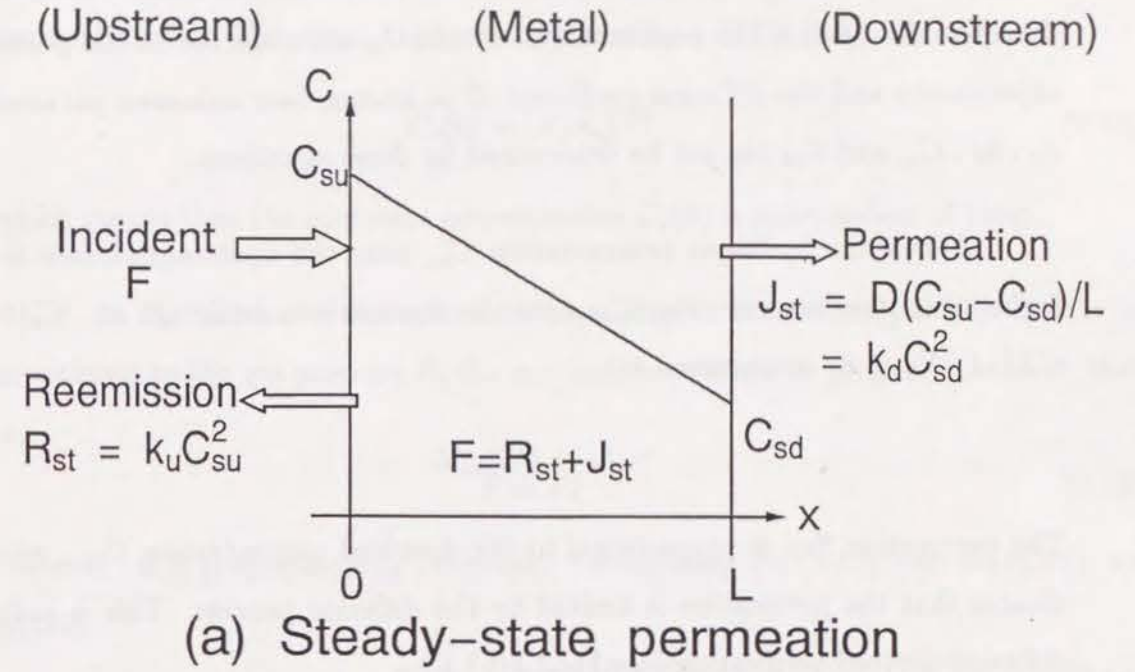


Fig. 2.1. Schematic drawings of the boundary conditions for hydrogen permeation in metals at the steady-state in (a) the general permeation and (b) the diffusion-limited permeation.

The equations of (1.6) through (1.8) contains seven parameters except for the thickness L . Even if the parameters of F and J_{st} are observed in the permeation experiments and the diffusion coefficient D is known, four unknown parameters of k_u , k_d , C_{su} and C_{sd} can not be determined by these equations.

When the hydrogen concentration C_{su} near the upstream surface is much higher than the concentration C_{sd} near the downstream surface, i. e. $C_s(0, t) \gg C_s(L, t)$, Eq.(1.6) is expressed as

$$J_{st} = DC_{su}/L \quad (2.11)$$

The permeation flux is proportional to the dissolved concentration C_{su} , which indicates that the permeation is limited by the diffusion process. This is called the diffusion-limited permeation (see Fig.1.1(b)).

In the diffusion-limited permeation, C_{su} can be obtained from Eq.(1.11) when J_{st} is measured and D is known. The recombination coefficient k_u on the upstream surface is also given from the value of F using Eqs.(1.9) and (1.10). On the other hand, the recombination coefficient k_d on the downstream surface can not be determined uniquely, since the value of C_{sd} in Eq.(1.8) is unknown.

It should be mentioned that Eq.(1.9) is not always approximated by $F = k_u C_{su}^2$ in the diffusion-limited permeation. When $k_u \ll k_d$, the first term of the right side in Eq.(1.9) might be smaller than the second term.

The boundary conditions of Eqs.(1.3) and (1.4) are also applied to the classical GDP (gas driven permeation) in which the steady-state permeation is expressed by Eq.(1.3). It has been considered in the classical GDP that the hydrogen concentration near the surface is in quasi-equilibrium with the hydrogen gas of the pressure P . If there is a complete equilibrium between the dissolved hydrogen and the hydrogen gas, no practical flows exist and hydrogen can not permeate. In the quasi-equilibrium,

the incident flux is nearly equal to the reemission flux and much larger than the permeation flux. Therefore, the boundary condition of Eq.(2.3) is rewritten by

$$C_s(0) = (F/k_u)^{1/2} \quad (2.12)$$

which means that the upstream concentration $C_s(0)$ is independent of time.

As the number of the molecules impinging to the surface per unit time is in proportion to the gas pressure P , the incident flux should be proportional to P , that is,

$$F = P\xi \quad (2.13)$$

where ξ is a proportionality constant. Substituting Eq.(2.13) into Eq.(2.12), we obtain

$$C_s(0) = (\xi/k_u)^{1/2} P^{1/2} \quad (2.14)$$

When a parameter K is defined here by

$$K = (\xi/k_u)^{1/2} \quad (2.15)$$

Eq.(2.14) becomes the same as Sieverts' law (Eq.(1.2)) and the parameter K is the solubility.

The hydrogen concentration near the downstream surface faced to vacuum is considered to be zero in the quasi-equilibrium. This means that $C_s(L, t)$ given by Eq.(2.4) is always much smaller than the concentration $C_s(0)$ near the upstream surface.

From above results, the boundary conditions on the upstream and the downstream surfaces are

$$C_s(0) = C_{su} = KP^{1/2} \quad (2.16)$$

$$C_s(L) = C_{sd} = 0 \quad (2.17)$$

respectively. Combining Eqs.(2.6), (2.16) and (2.17), the permeation flux J_{st} at the steady state is given by

$$J_{st} = DK \frac{P^{1/2}}{L} \quad (2.18)$$

As the product of the diffusion coefficient D and the solubility K is the permeation coefficient Φ (see Eq.(1.4)), Eq.(2.18) is just the same as Eq.(1.3). In this way, the Richardson's equation which describes the classical GDP is derived.

The equation (2.18) can be written as

$$J_{st} = DC_{su}/L \quad , \quad (2.19)$$

which is the same as Eq.(2.11). This means that the classical GDP is always limited by the diffusion process.

2.2 Equations for traps

For analyzing experimental results to obtain the concentration of the traps and the trapping energy, a model concerned with the trapping and detrapping of hydrogen is required. A diffusion equation with a single trap was first given by McNabb and Foster [98]. It is written in a one-dimensional form by,

$$\frac{\partial C_s(x,t)}{\partial t} = D \frac{\partial^2 C_s(x,t)}{\partial x^2} - \frac{\partial C_t(x,t)}{\partial t} \quad , \quad (2.20)$$

where $C_t(x,t)$ is the hydrogen concentrations in the traps. The parameter $C_s(x,t)$ is the dissolved hydrogen concentration as mentioned before and represents the hydrogen concentration in solution sites. As no hydrogen in the traps would be emitted directly from the surface, the boundary conditions of Eqs.(2.3) and (2.4) are also used here.

The term $\partial C_t / \partial t$ in Eq.(2.20) represents the time-dependent change in the concentration of trapped hydrogen. Equations to describe the term have been given

by Wilson and Baskes [83], Myers et al. [91] and Doyle and Brice [68]. Their equations are essentially the same but slightly different in details. Here a new equation was derived, which covered all of them as will be shown later.

The plasma-facing walls are bombarded with fast neutrons and heliums, the traps would be associated with lattice defects and bubbles. One kind of traps associated with point defects was assumed here. The trap associated with bubbles will be discussed in 6.5.

The following assumptions were made for hydrogen diffusion and trapping to derive the equations. A potential diagram of interstitial sites for dissolved and trapped hydrogen in metals is shown in Fig.2.2, which is concerned with the assumptions of 1, 2, 3 and 5.

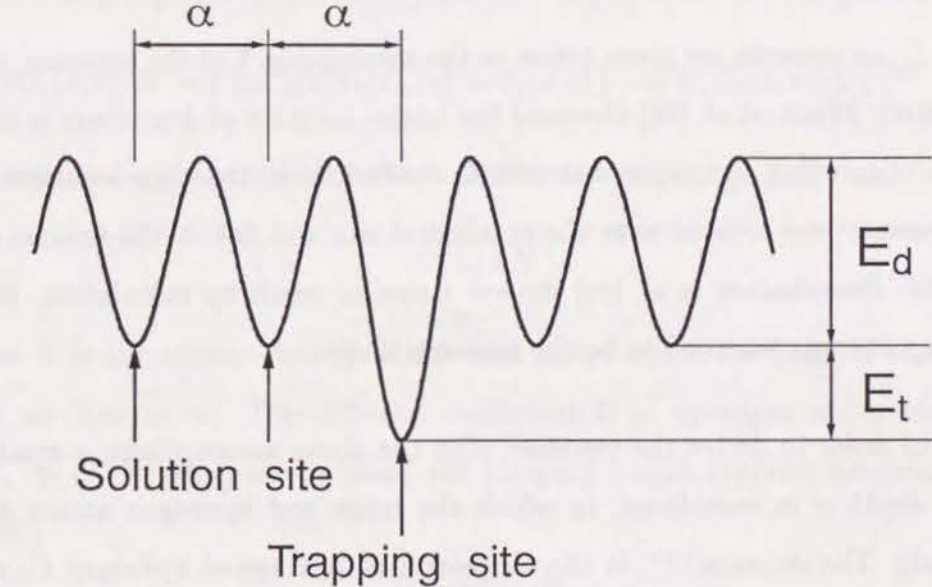


Fig. 2.2. Potential diagram of interstitial sites for dissolved and trapped hydrogen in metals.

1. Hydrogen is located as atom in either a solution site or a trapping site. Both the sites are interstitial.
2. A hydrogen atom diffuses by jumping from one site to the nearest neighbor sites. The jump length is the nearest neighbor distance α .
3. When a hydrogen atom goes into or escapes from the trapping site by a jump, the jump length is equal to α .
4. One trapping site can trap one hydrogen atom.
5. The enthalpy of hydrogen in the trap is lower by E_t than that in solution. The energy E_t is defined as the trapping energy.
6. Neither the trapping site nor the combined hydrogen-trap pair diffuses.
7. The density C_o of the trapping site is much lower than that of the solution site C_a , that is, $C_o \ll C_a$.
8. The concentration C_s of hydrogen in solution is much lower than C_a ($C_s \ll C_a$).
9. The trap density C_o is independent of time.

Some remarks are given below to the assumption 1 of the trapping site being interstitial. Myers et al. [91] observed the lattice location of deuterium in iron using the ion channeling technique. At 200 K, deuterium in the trap associated with a monovacancy was located near the octahedral site and not in the nearest neighbor host site. Besenbacher et al. [99] showed a similar result by calculation. Hence the trapping site was assumed to be the interstitial site.

In order to derive the equation with the above assumptions, a small volume at the depth x is considered, in which the traps and hydrogen atoms distribute uniformly. The increase C^+ in the concentration of trapped hydrogen $C_t(x, t)$ in a short time Δt is the product of the following four terms: a jumping rate $Y\omega\Delta t$ for a dissolved hydrogen to neighbors in Δt , the probability $C_o(x)/\{C_o(x) + C_a\}$ that the neighbor is a trapping site, the probability $\{C_o(x) - C_t(x, t)\}/C_o(x)$ that the trapping site is empty and the concentration $C_s(x, t)$ of dissolved hydrogen, where

Y is the number of the nearest neighbor sites, ω is the jumping rate for a dissolved hydrogen in a unit time. Considering the above assumption 7 of $C_a \gg C_o$, C^+ is written by,

$$C^+ = Y\omega C_s(x, t) \{C_o(x) - C_t(x, t)\} \Delta t / C_a \quad (2.21)$$

Similarly, the decrease C^- in the concentration of trapped hydrogen is the product of the following four terms: a jumping rate $Y\omega'\Delta t$ for a trapped hydrogen to neighbors in Δt , the probability $C_a/\{C_o(x) + C_a\}$ that the neighbor is a solution site, the probability $\{C_a - C_s(x, t)\}/C_a$ that the solution site is empty, and the concentration $C_t(x, t)$ of hydrogen in the traps, where ω' is the jumping rate for a trapped hydrogen in a unit time. The assumptions of 7 ($C_a \gg C_o$) and 8 ($C_a \gg C_s$) give

$$C^- = Y\omega' C_t(x, t) \Delta t \quad (2.22)$$

Using Eqs.(2.21) and (2.22), the time dependence of C_t is given by,

$$\partial C_t(x, t) / \partial t = Y[\omega C_s(x, t) \{C_o(x) - C_t(x, t)\} - \omega' C_a C_t(x, t)] / C_a \quad (2.23)$$

The density C_a of the solution site is expressed by

$$C_a = hN \quad (2.24)$$

where N is the atomic density of the host metal and h the number of the solution sites per host atom. The diffusion coefficient D of hydrogen under the condition of $C_a \gg C_s$ is expressed by using the jumping length (nearest neighbor distance) α [100];

$$D = \alpha^2 Y \omega / 6 \quad (2.25)$$

A parameter is introduced, which is defined by $f \equiv \omega' / \omega$. This is equal to $\exp(\Delta G / kT)$ [100], where k is the Boltzmann constant, T is the absolute temperature of the metal and ΔG is the difference in the free energies between the trapped and

Table 2.1. Values of $6/hN\alpha^2$ represented by the lattice constant a

metal	fcc		bcc	
site	Octahedral	Tetrahedral	Octahedral	Tetrahedral
h	1	2	3	6
α	$a/\sqrt{2}$	$a/2$	$a/2$	$a/2\sqrt{2}$
N	$4/a^3$		$2/a^3$	
$6/hN\alpha^2$	$3a$		$4a$	

dissolved hydrogens. The difference in the enthalpies between them is $-E_t$ (E_t : the trapping energy) under the assumption 5. The difference in the entropies is written by ΔS . Consequently, f is given by the form

$$f = \mu \exp(-E_t/kT) \quad , \quad (2.26)$$

where μ is $\exp(\Delta S/k)$ and independent of temperature T . The parameter μ has the same meanings as used in Doyle's equation [68] and represents a jumping ratio of the trapped to the dissolved hydrogen.

Combined with Eqs.(2.24) to (2.26), Eq.(2.23) is rewritten as

$$\frac{\partial C_t(x,t)}{\partial t} = \frac{6D}{hN\alpha^2} [C_s(x,t)\{C_o(x) - C_t(x,t)\} - hNfC_t(x,t)] \quad . \quad (2.27)$$

This is the general expression for the concentration change in trapped hydrogen with time. The term $6/hN\alpha^2$ in Eq.(2.27) depends on the structure of metals, which is represented by the lattice constant a as listed in Table 2.1. The interstitial sites in fcc and bcc metals are illustrated in Fig.2.3.

The equation (2.27) will be compared with the others equations. Doyle's equation [68] is expressed as

$$\frac{\partial C_t(x,t)}{\partial t} = 4\pi R_T D [C_s(x,t)\{C_o(x) - C_t(x,t)\} - hNfC_t(x,t)] \quad , \quad (2.28)$$

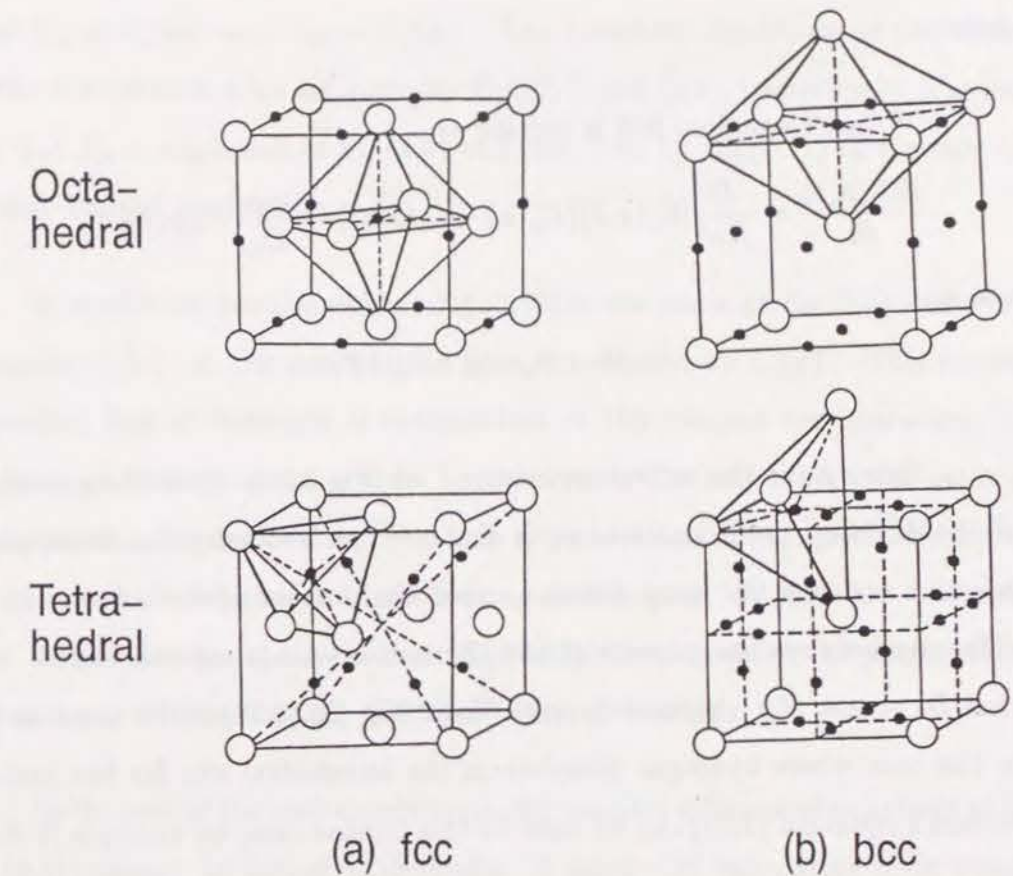


Fig. 2.3. Interstitial sites of octahedral sites (O) and tetrahedral sites (T) in (a) fcc and (b) bcc lattices. Large open circles and small closed circles represent the lattice host atoms and the interstitial sites, respectively.

where R_T is the effective trap radius and the parameter f is given by Eq.(2.26). Myers' equation [91] coincides with Doyle's equation when the parameter μ in Eq.(2.26) is unity. Their equations are the same as Eq.(2.27) when the value of R_T is taken as $3a/4\pi$ for fcc metals and a/π for bcc metals.

The effective trap radius R_T is derived from the theory of the diffusion-limited precipitation in metals [101]. No explanations for applying this macroscopic phenomenon to the hydrogen trapping have been given by either Doyle or Myers. It would be better to use Eq.(2.27) in the case of the traps associated with point

defects.

Wilson's equation [83] is written as

$$\frac{\partial C_t(x,t)}{\partial t} = \frac{D}{N\alpha^2} [C_s(x,t)\{C_o(x) - C_t(x,t)\} - \frac{\nu_0\alpha^2}{D_0\mu} C_t(x,t)] \quad , \quad (2.29)$$

where,

$$D = D_0 \exp(-E_d/kT) \quad . \quad (2.30)$$

Here, E_d is the activation energy (see Fig.2.2), D_0 is the pre-exponential of the diffusion coefficient and ν_0 is the attempt frequency for detrapping. This equation includes the jump distance α but the number of the solution sites or the difference between the interstitial and the lattice sites is not considered. Assuming that $D_0 = \nu_0\alpha^2/6\mu$ by analogy with Eq.(2.25), Eq.(2.29) is the same as Eq.(2.27) in the case where hydrogen dissolves in the tetrahedral site for bcc metals. The Wilson's equation (2.29) can be used for this limited case, for example H-Fe system.

In the present work, the sample metal was nickel, in which hydrogen was considered to solute in an octahedral site [29, 93]. From Table 2.1, Eq.(2.27) gives

$$\frac{\partial C_t(x,t)}{\partial t} = 3aD[C_s(x,t)\{C_o(x) - C_t(x,t)\} - NfC_t(x,t)] \quad , \quad (2.31)$$

where a is the lattice constant. This equation will be used to analyze our experimental data.

2.3 Solution of the equations

The solutions of coupled differential equations of (2.20) and (2.31) at the steady state are,

$$C_s(x) = C_{su} + (C_{sd} - C_{su})x/L \quad , \quad (2.32)$$

$$C_t(x) = C_s(x)C_o(x)/\{C_s(x) + Nf\} \quad , \quad (2.33)$$

where $C_{su} = C_s(0)$ and $C_{sd} = C_s(L)$. The boundary conditions of the upstream and the downstream sides are given by Eqs.(2.7) and (2.8), respectively. The permeation flux J_{st} is expressed as Eq.(2.6) and rewritten by Eq.(2.11) in the case of the diffusion-limited permeation.

It should be mentioned that Eq.(2.32) is the same as Eq.(2.5) and the concentration $C_s(x)$ at the steady state does not depend on $C_t(x)$. This means the permeation flux of hydrogen is independent of the trapped concentration $C_t(x)$. The term of "steady state" will be used below in the case where the permeation flux becomes a constant value. The trap concentration $C_o(x)$ gradually increased with the dose of the bombardment ions as shown later. In this case, the value of $C_t(x)$ would change rapidly to meet Eq.(2.33). Consequently, the permeation flux was constant. And we can say the "steady state" was kept.

In the case of the non-steady state, the coupled differential equations of (2.20) and (2.31) cannot be solved analytically. A numerical calculating code using the Gauss-Seidel method was developed. The code calculates the hydrogen concentrations of $C_s(x,t)$ and $C_t(x,t)$. The permeation flux is given by Eq.(2.2).

Chapter 3

Plasma driven permeation from rf plasmas

In this chapter, experiments on the PDP were performed using small rf-plasma devices with glass discharge tubes. Transient behaviors of the PDP were also studied experimentally and numerically.

3.1 Characteristics of plasma driven permeation at steady state

3.1.1 Experimental device

A schematic drawing of the rf-plasma device for the PDP experiments is shown in Fig.3.1. The upstream system, which contains a glass discharge tube, is evacuated by a diffusion pump. Hydrogen gas is continuously fed into the tube so as to keep the constant gas pressure in it. A quadrupole mass analyzer (QMA) for measuring permeated gas of hydrogen is set in the downstream system, which is evacuated by a turbo molecular pump (TMP). A sample membrane is put between the upstream and the downstream systems and heated by an ohmic heater. The temperature of the sample is monitored by a thermocouple directly contact with the sample.

A hydrogen plasma is produced by applying a radio frequency (rf) to coils which surround the discharge tube. A potential of the plasma can be varied from -1.5 kV to 1.5 kV by applying a probe voltage V_p to a probe in the tube. As the sample is electrically isolated, ion currents can be measured to monitor the amount of charged particles impinging to the sample. The incident flux of the particles, however, cannot be determined since electron and neutral particles as well as the

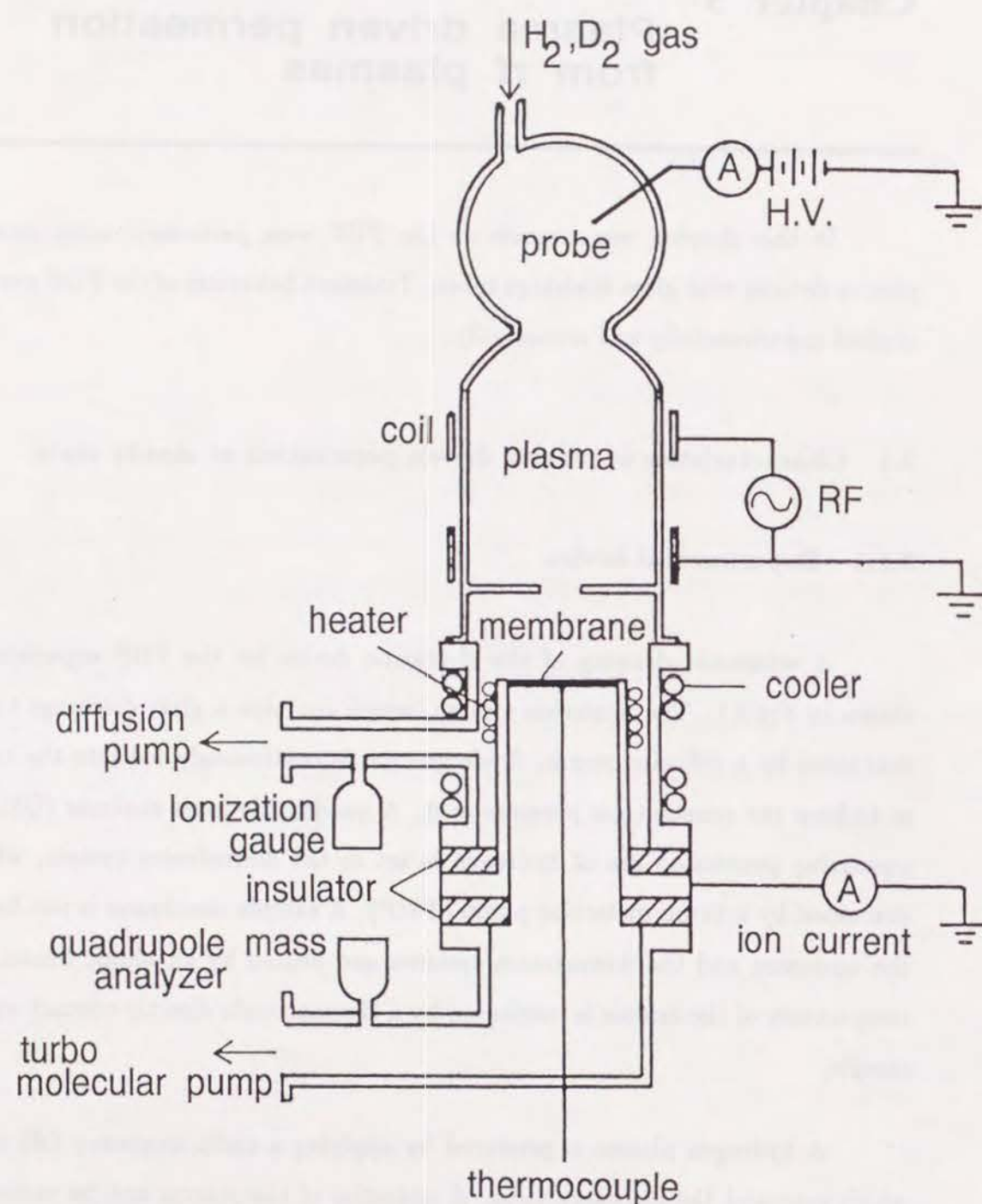


Fig. 3.1. Schematic drawing of the experimental device using rf-discharge in a glass tube.

charged particles come into the sample and the constitution of the charged particles such as D^+ , D_2^+ and D_3^+ is unknown.

3.1.2 Effect of the plasma

An example of the deuterium PDP through a type 304-stainless steel sample is shown in Fig.3.2. The thickness and the diameter of the sample were 0.05 mm and 35 mm, respectively. Prior the experiment, the sample was baked out at a temperature of 703 K for 3 hours. After that, the temperature was kept 663 K and the deuterium gas with a pressure of 0.8 Pa was fed to the tube. The permeation flux from the deuterium gas, i.e. the GDP, was less than a detection limit (0.001 in the arbitrary unit in the figure) of the QMA.

At the first cycle of the experiment, the rf plasma was discharged with $V_p = 0$. The permeation flux increased rapidly after a time lag of around 10 s. This increase continued for a few minutes until the permeation flux was almost saturated. The saturated value was about 2 in the arbitrary unit of the figure. It was at least two thousand times as large as that in the GDP where the plasma was not discharged. When the discharge was stopped, the permeation flux decreased toward zero. The noticeable PDP from the deuterium plasma was observed.

Both the PDP and the GDP would contribute to the permeation from the deuterium plasma since the gas was weakly ionized and molecules in the gas phase as well as energetic particles came into the sample. The very large ratio of the permeation flux to that in the GDP indicated that the contribution of the GDP was negligibly small compared to that of the PDP. Hence, the permeation from the plasma could be regarded as the PDP.

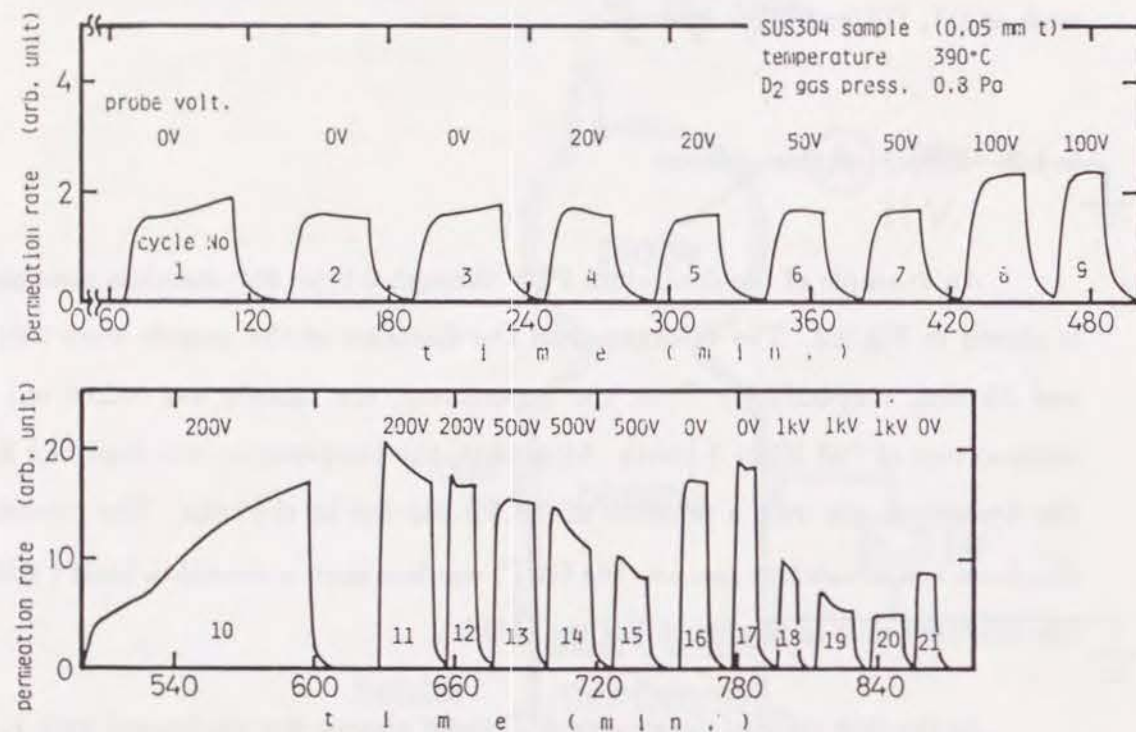


Fig. 3.2. Typical data showing the deuterium permeation fluxes of the PDP through type 304 stainless steel for successive changes in the probe voltage.

3.1.3 Dependence on probe voltage

The sequence of the start and the stop of the discharge was repeated under various values of V_p as shown in Fig.3.2. The permeation flux was nearly independent of V_p which was below 50 V. At the cycle of No.10 with $V_p = 200$ V, the permeation flux at the steady state became ten times larger than the previous values. As the ion current was kept constant of 0.3 mA during the experiments, the incident flux would not be changed. Implantation effects were not responsible for the increase of the permeation in the cycle No.10, since the permeation flux decreased with increasing V_p as shown in the cycles of No.11 to 15.

The permeation fluxes at the steady state in the cycles of No.16 and 17 were

about ten times larger than that in the cycles of No.1 to 3 under the same probe voltage of zero. The permeation flux would increase with decreasing the recombination coefficient on the upstream surface as will be discussed in the chapter 4. The increase in the permeation flux in the cycle No.10 was due to a decrease in the recombination coefficient on the upstream surface. This decrease would be caused by surface impurities which were desorbed from the inner walls of the discharge tube and absorbed or implanted to the sample.

In the cycles of No.11, 14 and others where the values of V_p were relatively high, the permeation flux decreased with time during the exposure of the plasma. This decrease is called as a permeation spike [56, 57, 60, 102]. The permeation spike is considered to indicate the decrease in the amount of impurities on the upstream surface as will be discussed in the chapter 4.

3.1.4 Contribution of neutral particles

A similar experiment as in 3.1.3 was performed with a 0.1-mm thick nickel sample at a temperature of 638 K and a deuterium gas pressure of 1.2 Pa. The permeation flux of the deuterium PDP was observed under some values of V_p while the rf discharge was continued. The result is shown in Fig.3.3.

There were no changes in the permeation flux when the probe voltage V_p was switched from 0 to -500 V. When V_p was negative, positive ions were attracted to the probe and scarcely impinged to the sample. These indicated that positive ions from the plasma did not much contribute to the PDP in this experiment. Neutral atoms produced in the plasma would mainly contribute to the PDP.

The permeation flux was smaller in the case of V_p being positive than that of $V_p = 0$ as shown in Fig.3.3, while the recombination coefficient would not be

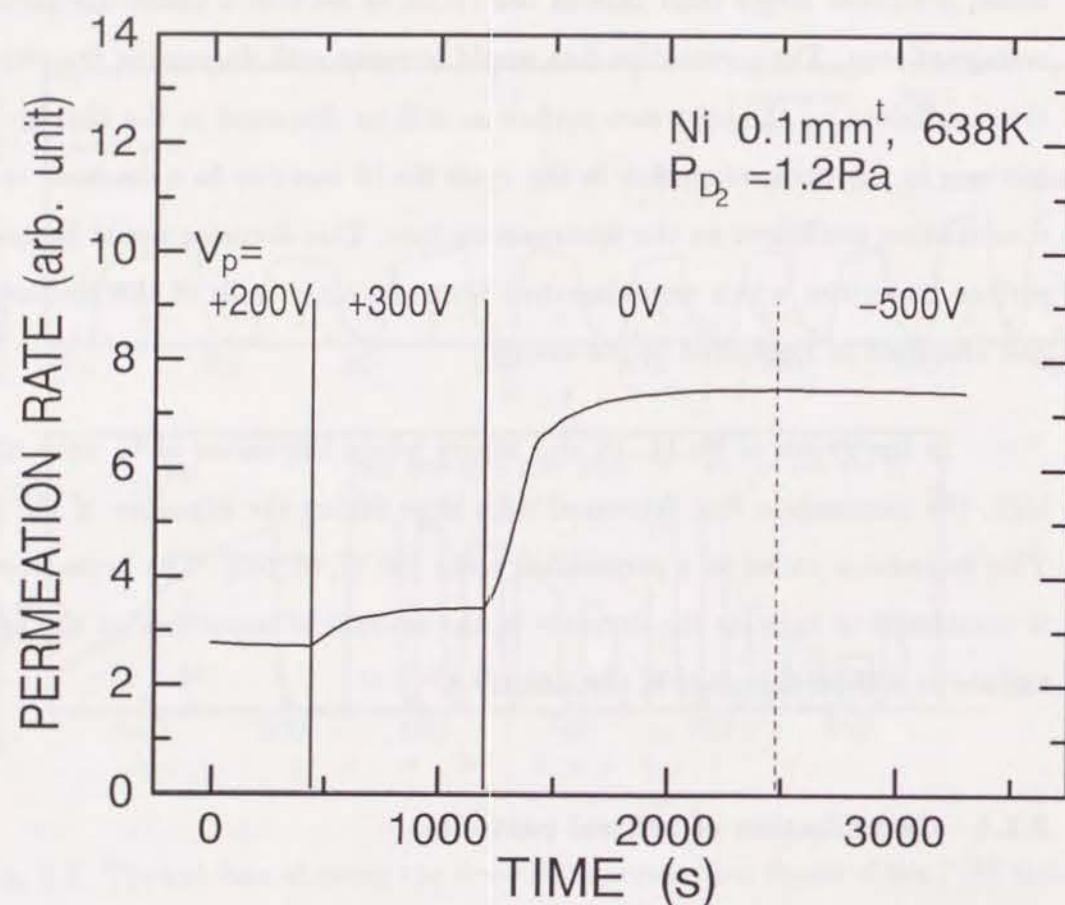


Fig. 3.3. Dependencies of the plasma driven permeation flux on various probe voltages.

changed considering no permeation spikes. It was probably because that electrons in the plasma were attracted to the probe and the neutral particles produced by electrons (Franck-Condon atoms) decreased.

3.1.5 Isotope effect

The isotope effect on the GDP is already known to be around the square root of the mass ratio as mentioned in the chapter 1. The isotope effect between hydrogen

and deuterium on the PDP was experimentally studied.

A 0.1-mm thick nickel membrane was exposed to a rf plasma of mixed hydrogen and deuterium gases under $V_p = 0$. The gas pressure was 1.2 Pa and the partial pressure of each gas was the same. The sample temperature was changed between 373 and 723 K. After the permeation fluxes of the PDP reached the constant values, the partial pressures of the permeated gases of H_2^+ , HD^+ and D_2^+ were observed by the QMA. There were assumed to be no monoatomic ions such as H^+ and D^+ .

A separation factor $\alpha_{sep}(T)$ at the sample temperature of T is defined here by

$$\alpha_{sep}(T) = \frac{\text{H/D ratio in permeated gas}}{\text{H/D ratio in fed gas}} \quad (3.1)$$

The experimental results of the separation factor are shown in Fig.3.4. The separation factor was found to be independent of the temperature and expressed as

$$\alpha_{sep}(T) = 1.26 \pm 0.06 \quad \text{for } 373K \leq T \leq 723K \quad (3.2)$$

Various processes would contribute to the separation factor such as diffusion and permeation in the sample, and ionization and neutral atom production in the plasma. The separation factor obtained above would depend not only on properties of the sample but on the experimental device and conditions. Nevertheless the separation factor α_{sep} of 1.26 was not so different from the square root of the mass ratio ($M_D/M_H = 1.41$). The isotope effect in the PDP was nearly the same as in the GDP.

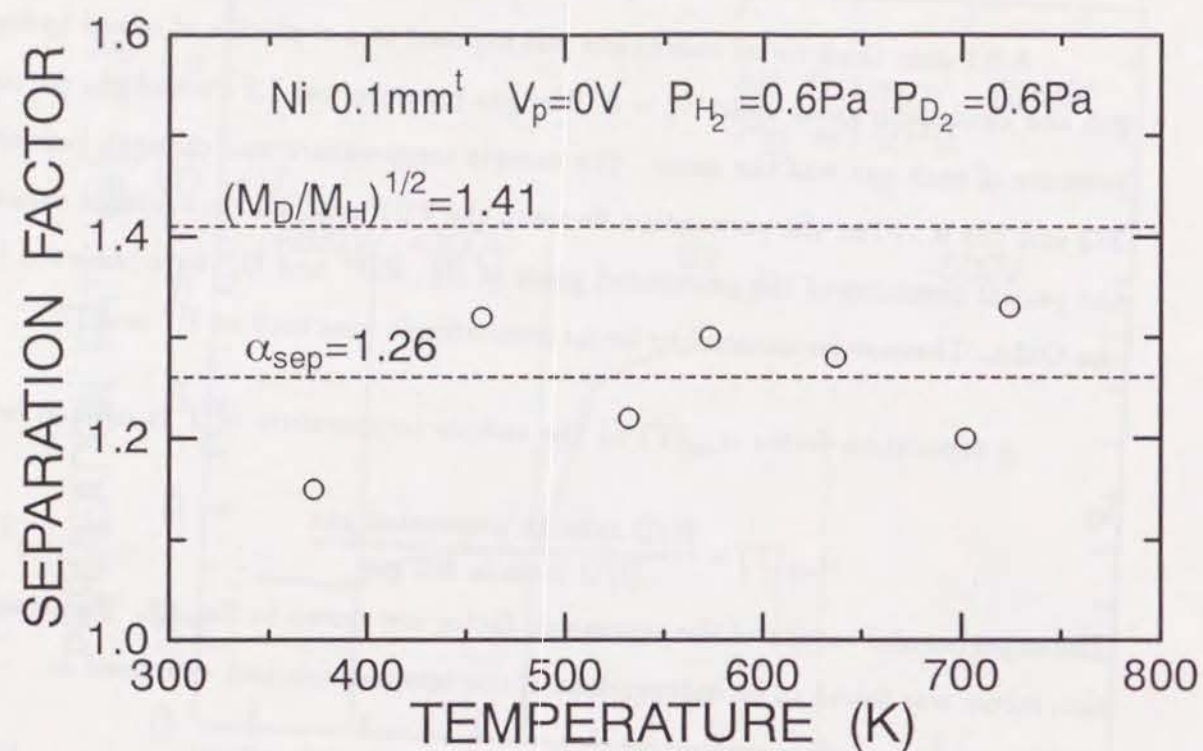


Fig. 3.4. Separation factor between hydrogen and deuterium for plasma driven permeation through a 0.1-mm thick nickel membrane.

3.2 Plasma driven permeation at non-steady state

A characteristic time in which hydrogen diffuses through a membrane with a thickness of L is usually represented as the time-lag [103]. It is defined by

$$\tau = L^2/6D \quad , \quad (3.3)$$

where D is the diffusion coefficient of hydrogen. In the case of a 0.1-mm thick nickel membrane at a temperature of 523 K, the time-lag of deuterium is 26 s using the value of D being $6.4 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ [104]. Duration times of the large plasma devices are generally short. For example, the typical duration times for the ICRF- and the NBI-operations of Heliotron E are 40 and 200 ms, respectively. They are

much shorter than the time-lag of 26 s in the above case. There have been little known about transient behaviors of the hydrogen permeation when the membrane are exposed to such short pulse plasmas. These behaviors were experimentally studied using a small plasma device shown in Fig.3.5.

3.2.1 Rf-plasma device for pulse exposure

The device is similar to that was used in the previous section. It consists of two vacuum chambers, the upstream and the downstream ones, separated by a nickel membrane. Both the chambers are evacuated by turbo molecular pumps to the pressure of 10^{-5} Pa for the upstream and 10^{-6} Pa for the downstream. The QMA in the downstream chamber monitors the permeation flux of deuterium.

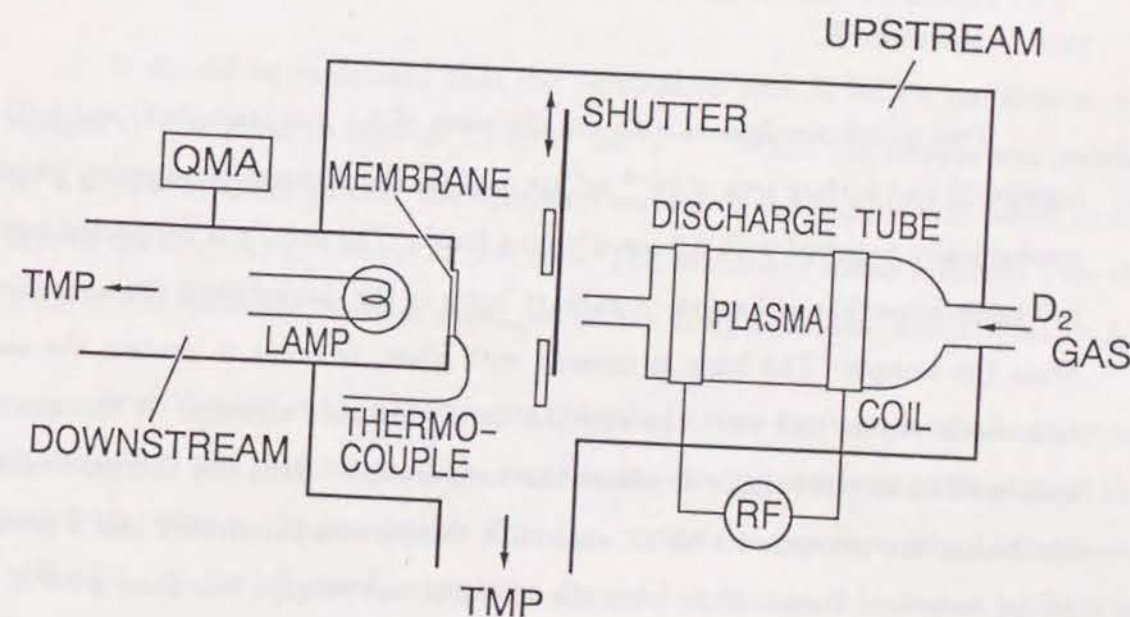


Fig. 3.5. Schematic drawings of the small plasma device for the pulse-exposure experiment.

A glass discharge tube is placed in the upstream chamber as shown in Fig.3.5. Deuterium gas, of which the flow rate is regulated by a leak valve, is fed into the tube. The plasma is produced by applying a radio frequency (rf) to deuterium gas.

As the membrane is exposed to neutral atoms as well as charged ions from the rf plasma, the incident particle flux is difficult to be measured. Hence, the pressure of deuterium gas introduced in the discharge tube is monitored as a substitute for the incident flux. Typical gas pressure and the rf power are 5.3 Pa (40 mtorr) and 20 W, respectively.

In order to control the exposure time in which the sample is exposed to the plasma, a mechanical shutter is set between the sample and the tube. The shutter is opened at $t = 0$ and closed at $t = t_e$ in the experiments. The time t_e represents the exposure time. It is measured by a video camera through a glass window. The shortest exposure time is 0.2 s, which is the same orders of magnitude of the duration time of Heliotron E.

Two nickel membranes with the thickness of 0.1 mm (sample 1) and 0.03 mm (sample 2) and surface area of 10^{-3} m^2 are used for the permeation samples, which are mechanically polished with $0.3 \mu\text{m}$ alumina finish. The sample is supported between two knife-edge shaped flanges. A radiant lamp in the downstream chamber directly heats the sample. The lamp is covered with glass, in order to protect the sample from both vapors and electrons emitted by a resistance element. A thermocouple spot-welded to the sample monitors the temperature. Both the thermocouple and the heater are connected with an automatic temperature controller and a deviation of the measured temperature from the set value can be kept less than $\pm 0.5 \text{ K}$.

3.2.2 Pulse exposure experiments

The sample was a 0.03-mm thick nickel membrane and kept at 523 K. First, the steady-state permeation flux was observed while the shutter was opened. In the case of the GDP with the deuterium gas pressure of 5.3 Pa, the permeation flux was less than the detection limit of the QMA, which was $6 \times 10^{15} \text{ m}^{-2}\text{s}^{-1}$. When the deuterium gas was discharged under the above conditions, the permeation flux at the steady-state reached a value of $2.6 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$.

After the shutter was closed and the permeation flux reached a constant value, the shutter was opened for the exposure time of t_e . Evolution curves of the permeation flux under some values of t_e are shown in Fig.3.6. To avoid overlapping, the successive curves are displaced vertically. The results showed that rising shapes of the curves around $t = 0$ s were the same. The maximum value of the permeation flux increased with t_e until it reached the steady-state value at around 10 s.

It should be mentioned that the permeation flux J_0 before the shutter was opened ($t \leq 0$) was as high as $7.1 \times 10^{17} \text{ m}^{-2}\text{s}^{-1}$. When the sample was isolated by a copper cylinder so that the upstream surface of the sample only faced to the hole of the shutter, J_0 became almost zero. The deuterium atoms reflected from the walls of the upstream chamber impinged on the sample [52] and contributed to J_0 .

Several series of the experiments described above were conducted under some temperatures and thicknesses of the sample, and the gas pressures. The plots of the maximum value in the permeation flux J_{max} versus the exposure time t_e are shown in Fig.3.7. As the observed permeation flux at $t \geq 0$ was contributed by both of direct and reflected particles, the value of J_{max} was obtained by subtracting J_0 from the observed maximum permeation flux. The experimental conditions are written in the figure.

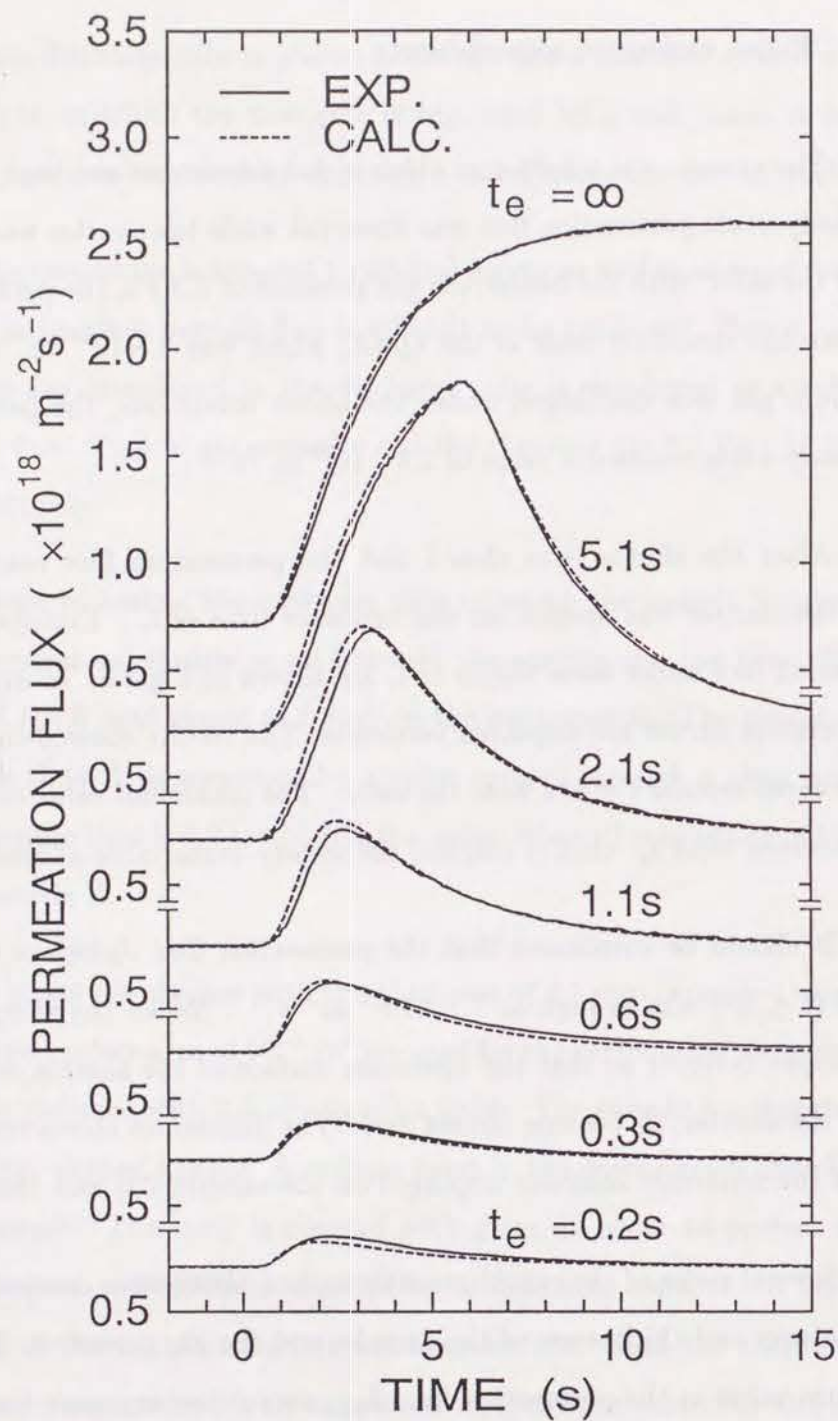


Fig. 3.6. Time-dependent changes in the permeation flux under some exposure times (solid lines). The successive curves are displaced vertically by one scale. Broken lines show the results of the numerical calculation.

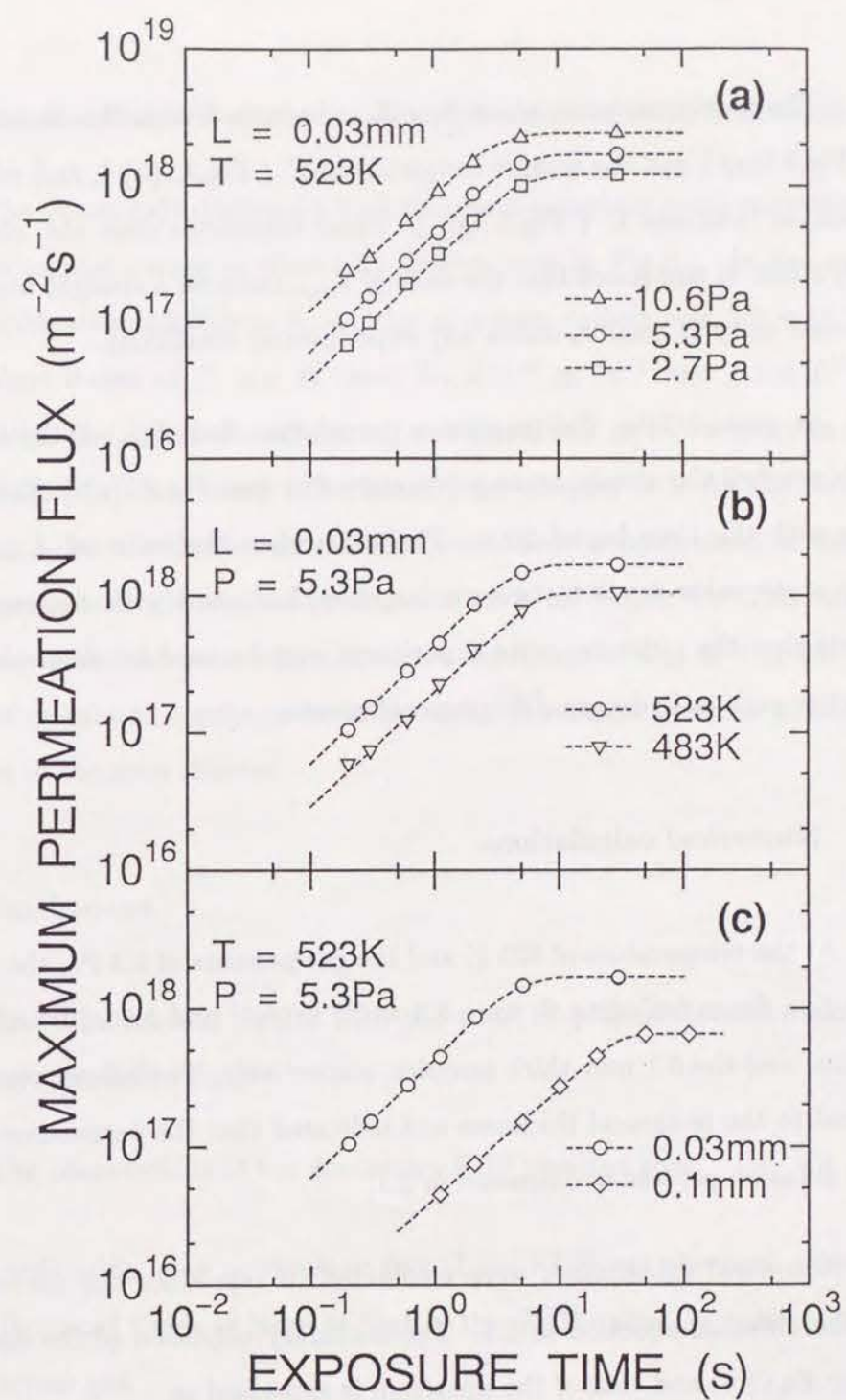


Fig. 3.7. Relations between the maximum permeation flux J_{max} and the exposure time t_e under various experimental conditions of (a) the gas pressure of deuterium P , (b) the sample temperature T and (c) the sample thickness L . Broken lines are guides for eyes.

The maximum permeation flux J_{max} increased with the deuterium pressure P (Fig.3.7(a)) and the sample temperature T (Fig.3.7(b)), and with decreasing the sample thickness L (Fig.3.7(c)). These tendencies were also observed at the steady state. It was found that the data of J_{max} came on a straight line with a slope of around unity at small t_e under any experimental conditions.

At around 31 s, the maximum permeation flux J_{max} of the 0.1-mm thick sample reached the steady-state permeation flux (see Fig.3.7(c)). This time nearly agrees with the time-lag of 26 s. The time when the value of J_{max} reaches the steady-state value tends to become larger with L , and with decreasing T . This suggests that the pulse exposure experiment may be used for determining physical properties such as hydrogen diffusion coefficients.

3.2.3 Numerical calculations

At the temperature of 523 K and the gas pressure of 5.3 Pa, the steady-state permeation fluxes including J_0 were $2.6 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$ and $1.0 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$ for the 0.03 mm- and the 0.1 mm-thick samples, respectively. The values were nearly proportional to the reciprocal thickness and indicated that the permeation was limited by the diffusion process as discussed in 2.1.

Numerical calculations were conducted to reproduce the curves in Fig.3.6 using the diffusion equation in 2.1. The boundary condition of the downstream is given by Eq.(2.4) and that of the upstream is expressed as

$$F = k_u C_s^2(0, t) - D(\partial C_s / \partial x)_{x=0} \quad \text{for} \quad 0 \leq t \leq t_e, \quad (3.4)$$

$$F_0 = k_u C_s^2(0, t) - D(\partial C_s / \partial x)_{x=0} \quad \text{for} \quad t \leq 0, \quad t \geq t_e, \quad (3.5)$$

where F and F_0 are the total incident flux during the shutter being opened and the incident flux of the reflected particles with the shutter being closed, respectively.

The permeation flux $J(t)$ at the non-steady state is obtained from Eq.(2.2).

The numerical calculations with the above equations could very well reproduce the experimental curves as shown by broken lines in Fig.3.6. In the calculations, the recombination coefficient k_u on the upstream surface was $3.3 \times 10^{-30} \text{ m}^4\text{s}^{-1}$, the incident fluxes of F and F_0 were $7.4 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$ and $1.1 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$, respectively. The diffusion coefficient D was $6.4 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ which was determined from the in-situ observation experiment (see chapter 5). As the recombination coefficient k_d on the downstream surface could not be determined in the diffusion-limited permeation, it was assumed to be $5.0 \times 10^{-25} \text{ m}^4\text{s}^{-1}$. This value assured the diffusion-limited permeation, i. e. the condition of $C_{su} \gg C_{sd}$ and it did not affect the calculated results so far as $k_u \ll k_d$. A relation between k_u and k_d will be discussed in the next chapter.

3.3 Conclusions

The experimental results with the small rf-plasma devices obtained in this chapter are the followings:

The observations of the deuterium PDP resulted that

1. The noticeable large permeation flux of the PDP was observed, which was over two thousand times as large as that in the GDP under the same pressure of the deuterium gas.
2. The steady-state permeation flux of the PDP depended on histories of the plasma exposure to the sample. It was probably attributed to the behavior of the impurities on the surface which was faced to the plasma.
3. Neutral atoms mainly contributed to the PDP while ions did not. This was supported by the fact that a large permeation flux was observed when the negative

potential was applied to the plasma.

4. The separation factor between hydrogen and deuterium was obtained. The isotope effect in the PDP was nearly the same as in the GDP.

From the pulse-exposure experiments on the deuterium PDP in nickel, it was concluded that

5. The permeation at the steady state was limited by the diffusion process.
6. When the sample was exposed to the deuterium plasma for short times, the maximum permeation flux J_{max} at the non-steady state was nearly proportional to the exposure time.
7. The maximum permeation flux J_{max} increased with the pressure of the discharged gas P and the sample temperature T , and with decreasing the sample thickness L . These tendencies were the same as those at the steady state.
8. The transient behaviors of the permeation flux could be well reproduced by the numerical calculations using the diffusion equations described in 2.1.

Chapter 4

Plasma driven permeation in Heliotron E

Many basic experimental studies have been made on the PDP using small plasma devices such as ion gun [56, 57, 60, 105], rf or RG discharge plasmas [44, 46, 102] and atomizer [52, 53, 55] as mentioned in the chapter 3. And the basic physical processes are known. Now in the stage of D-T experiments, advanced works are needed using fusion experimental devices, since their plasma parameters such as ion temperatures and densities are obviously much closer to those in fusion reactors and several diagnostic systems are available. Dynamic effects of the oxygen recycling [106, 107] on permeation will be more serious in these devices. However, there have been little works except for those by Shmayda et al. [108, 109] in TEXTOR.

The deuterium PDP was studied using one of the largest helical plasma devices, Heliotron E in Plasma Physics Laboratory of Kyoto University. As the result, the deuterium PDP from the steady-state plasma for the discharge cleaning was observed clearly and it was found that the permeation flux reflected dynamic behaviors of recycled particles such as deuterium and oxygen. The diagnosis of the discharge cleaning from the permeation flux will also be discussed.

4.1 Permeation cell in Heliotron E

Heliotron E is one of the largest helical systems of which the major radius is 2.2 m and the average minor radius of plasmas is 0.2 m. Detail descriptions of the device have been reported elsewhere [110, 111]. Currentless high temperature plasmas are obtained by 53.2 GHz electron cyclotron resonance heating (ECH) combined with neutral beam injection (NBI) or ion cyclotron range of frequency (ICRF). The major

components for the discharge and the heating are shown in Fig.4.1.

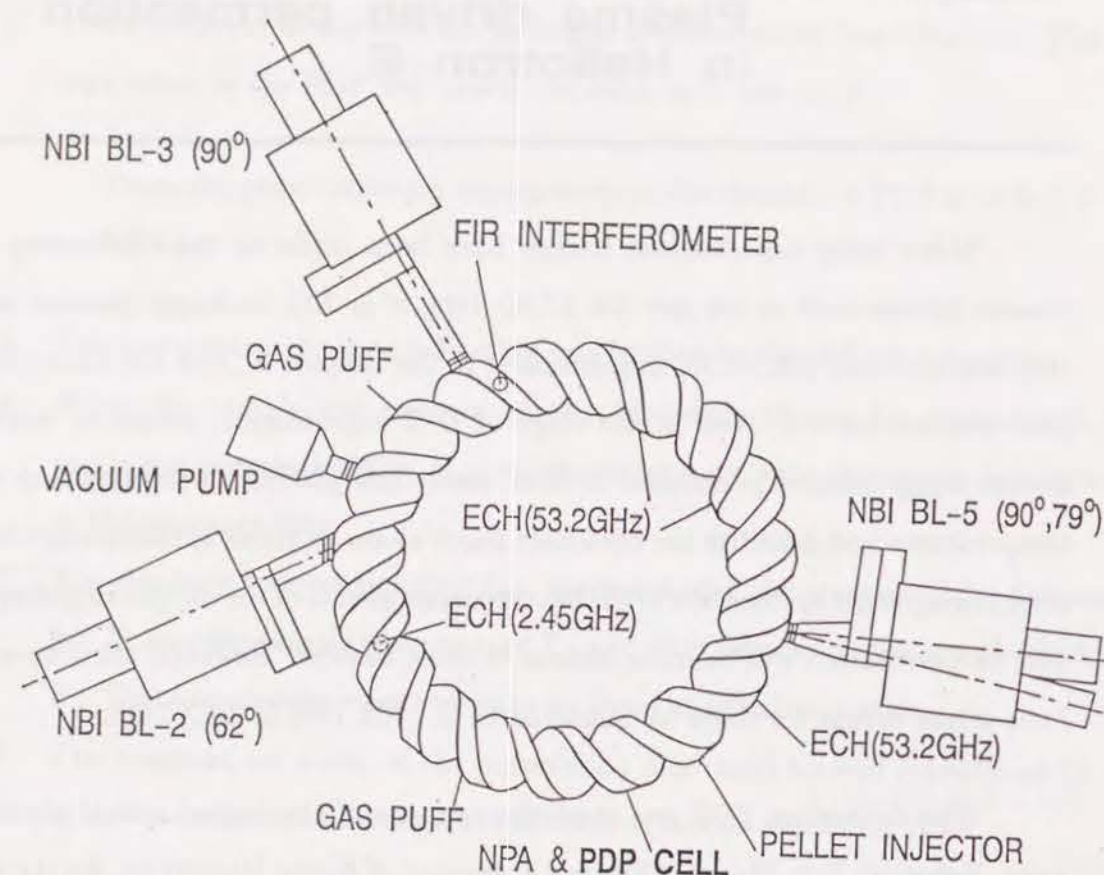


Fig. 4.1. The major components for the discharge and the heating of Heliotron E.

The 2.45 GHz ECH plasma with a steady-state confinement field is applied for the discharge cleaning of Heliotron E. The ECH power is 3 to 4 kW and the typical plasma density and the temperature are 10^{16} to 10^{17} m^{-3} and 1 to 10 eV, respectively [112]. Coatings such as titanium and carbon are not added to the first wall of stainless steels.

A permeation cell, in which the PDP is observed, is installed adjacent to the neutral particle analyzer (NPA) at the #17.5 outer port as shown in Fig.4.2. The cell was made of two ultra-high vacuum systems, the upstream and the downstream ones, separated by a metal membrane. Both the systems are evacuated by turbo molecular pumps to the pressure of 10^{-6} Pa. As the port is located behind the single-X point

of the separatrix of the magnetic field, the membrane is exposed mainly to neutral particles.

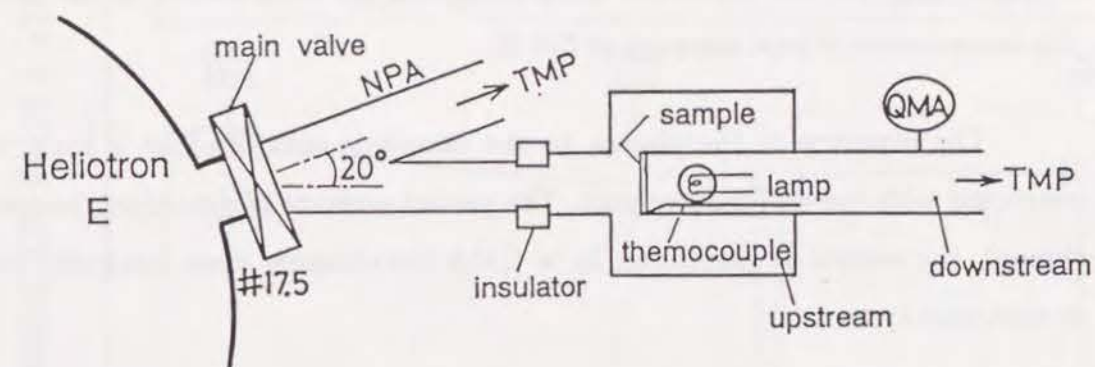


Fig. 4.2. Schematic drawings of the permeation cell installed at the #17.5 outer port of Heliotron E.

Studies on the deuterium PDP using the rf plasma in a glass tube have been made in our previous works [46, 69, 104, 113]. Through these studies, nickel membranes were showed to have a good reproducibility of the permeation. It is because that oxygen on the surface of nickel are easily removed and surface states with respect to the release of hydrogen are kept constant. Iron may be better for the permeation membrane, considering higher diffusivities of hydrogen in it. However, some cleaning devices [108] would be required to remove oxygen from the iron membranes, since iron is easily oxidized. Therefore, nickel is selected for the permeation membrane in this experiment for the sake of the simplicity of devices and the data reproducibility.

Two nickel membranes with the thickness of 0.1 mm (sample 1) and 0.03 mm (sample 2) and surface area of 10^{-3} m^2 are used for the permeation samples, which are mechanically polished with $0.3 \mu\text{m}$ alumina finish. The sample is supported between two knife-edge shaped flanges located 1.05 m apart from the center of the

plasmas. It faces to the core plasmas although it is placed at an angle of 20° to the surface normal.

A radiant lamp directly heats the sample, which is the same as in 3.2. A thermocouple spot-welded to the flange monitors the temperature of the sample. The temperature is kept constant at 523 K.

The exposure of the plasma to the sample is controlled by a main valve connected with the #17.5 outer port. The partial pressure of deuterium permeated through the sample is monitored by a QMA (quadrupole mass analyzer) in the downstream system.

4.2 Plasma driven permeation in discharge cleaning

Figure 4.3 shows an evolution of the deuterium permeation flux through the sample 1 during the deuterium discharge cleaning of Heliotron E. The pressure of deuterium gas in the chamber was first set to be 9×10^{-4} Pa. A voltage applying to a piezoelectric valve for the gas feed was kept constant to control the gas pressure. Adjustments of the valve were conducted twice during the discharge, which slightly influenced on the permeation flux as shown in Fig.4.3 by two small stepwise increases in the curve.

The operations of the plasma and the main valve between the permeation cell and Heliotron E, and the corresponding changes in the permeation flux are the followings:

1. the discharge on and the valve opened; the flux increased significantly, arrived at a maximum value, and then decreased gradually to reach an constant value.
2. the valve closed; the flux rapidly decreased toward zero.

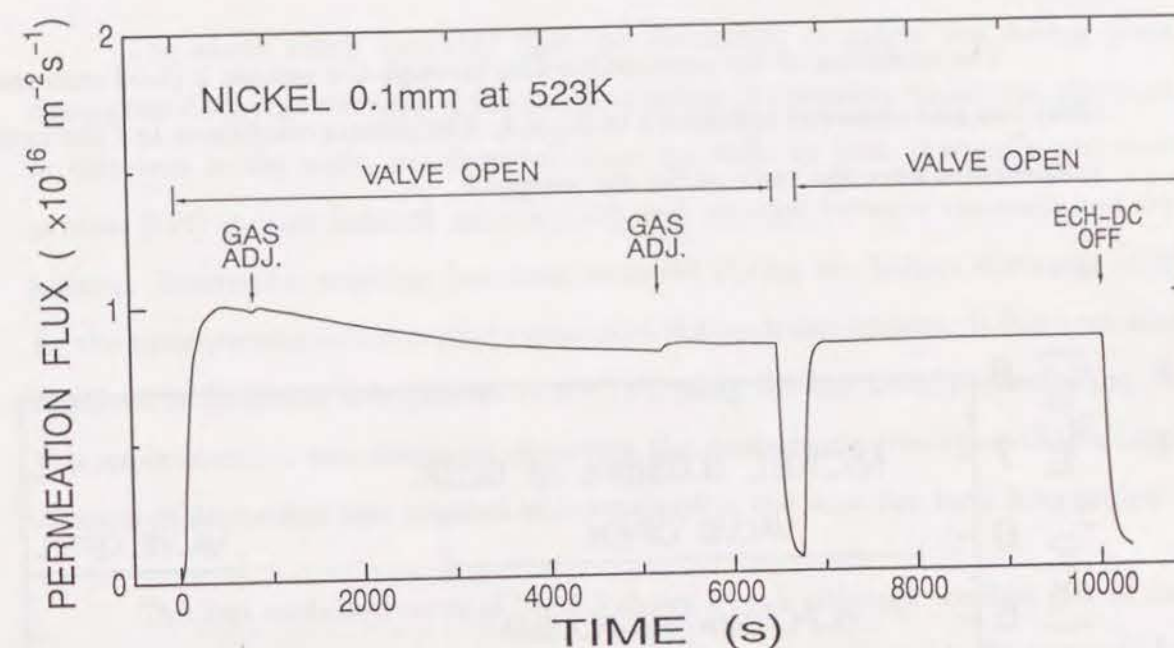


Fig. 4.3. Evolutions of the plasma driven permeation of deuterium in the 0.01-mm thick nickel membrane exposed to the ECH plasma.

3. the valve opened again; the flux reached the same value as observed just before the valve was closed.
4. the discharge off while the valve opened; the flux rapidly decreased toward zero in spite of the exposure of the membrane to deuterium molecules.

When the sample was exposed to deuterium molecular gas with the same pressure, the permeation flux of the GDP (gas-driven permeation) was less than $4 \times 10^{13} \text{ m}^{-2} \text{ s}^{-1}$. The maximum permeation flux of the PDP was $1.0 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$ as shown in Fig.4.3, which was at least 200 times larger than that of the GDP. A large effect of the plasma on the permeation was also observed in the large plasma device as well as in the small rf-plasma devices in the chapter 3.

4.3 Particle recycling

The evolution of the permeation flux through the sample 2 (0.03-mm thickness) was also observed and shown in Fig.4.4. The plasma conditions and the sample temperature were the same as for the sample 1.

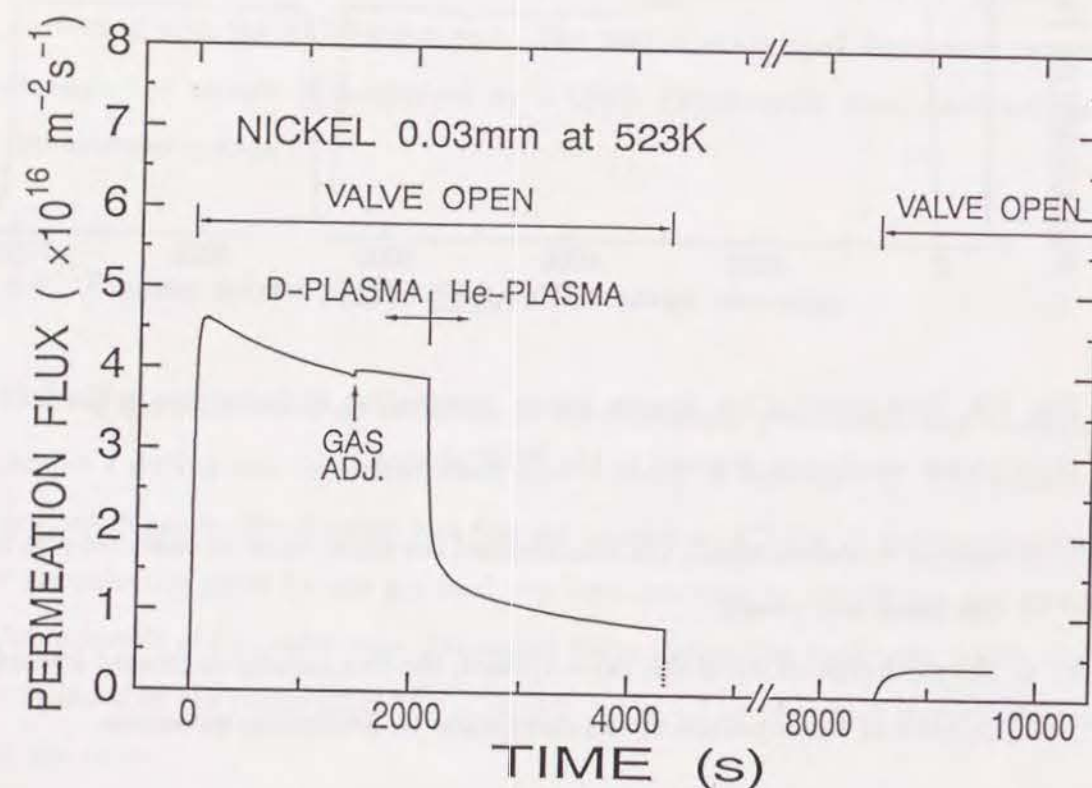


Fig. 4.4. Deuterium permeation flux in the 0.03-mm thick nickel membrane exposed to the deuterium plasma, and subsequently to the helium plasma.

The discharged gas was changed from deuterium to helium after about 2000 s from the valve opening. The deuterium permeation flux rapidly decreased at first as shown in Fig.4.4. Then approached to a constant value, but it never reached zero. It became zero when the valve was closed. When the valve was opened again at 8500 s, the permeation flux increased and reached a value which was about one tenth of

that observed for the deuterium plasma. It kept the constant value over 1000 s.

The above result indicated that the deuterium recycling was taking place during the discharge cleaning of the helium plasma. Deuterium, which was absorbed or dissolved in the walls, was desorbed from the walls by both thermally activated process [114] and ion induced process [115], and recycled between the walls and the plasma. Deuterium recycling has been observed during the helium discharge [116] by the measurement of the partial pressure in the upstream system. It has been also observed in Heliotron E by Kondo et al. [117] using the spectroscopic technique. In this experiment, it was shown by observing the deuterium permeation that a large amount of deuterium was recycled and remained in the chamber for a long period.

The first evolution curve in Fig.4.3 shows a peak although the flow rate of the feed gas was kept constant. A similar peak is also seen in Fig. 4.4. They would be permeation spikes [56,57,60,102]. The permeation spike is considered to be caused by changes in some characteristics of the membrane concerned with the release of hydrogen from metal surfaces. At the steady state, the incident flux of deuterium to one surface of the membrane is balanced by the reemission flux from the surface and the permeation flux from the other surface. Hence, the permeation spike corresponds to an increase in the reemission flux.

One of the possible causes of the enhanced reemission is the removal of impurities from the surface, since they suppress the release of hydrogen from the surface [70,73]. The main elements of the impurities in the plasma devices are oxygen and carbon [118]. Oxygen would be more effective between them. Carbon on the nickel surface less affects the permeation flux [119,120]. As the energy of the incident particle was no more than 10 eV, radiation damages [57] and the sputtering [60] were not responsible in this experiment.

The binding energy of oxygen to nickel is relatively small [121] and oxygen

is readily removed by exposures of energetic hydrogen particles [122]. The oxygen recycling has been observed in Heliotron E [107], as well as in other large plasma devices [106]. Hence, also in this experiment oxygen particles would exist in the chamber, and be fed to and removed from the membrane surface at the same time. The feed rate of oxygen would decrease with a progress of the cleaning, until it became balanced with the removal rate.

A characteristic time in which hydrogen diffuses through a membrane with a thickness of L is usually represented by the time-lag [103], which has been already mentioned in 3.2. In the case of this experiment, the time-lag τ of deuterium is obtained to be 26 s from Eq.(3.3), where the diffusion coefficient is $6.4 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ (see chapter 5). It is much smaller than the cleaning time. The permeation spikes in the first evolution curves in Fig.4.3 and Fig. 4.4 would represent the decrease in the amount of the recycled oxygen without a time lag.

Impurities in the residual gas are monitored by conventional methods such as QMA measurement. However, there are no useful ways to know the cleanliness on the plasma-facing walls. The PDP may be used for a diagnosis of the discharge cleaning on the walls, since the recombination coefficient is sensitive to the surface oxides [70, 73, 123]. When the permeation flux becomes the constant value, the impurities on the surface would not so much decrease. It is better to use not only the conventional QMA measurement but also the PDP measurement for the diagnosis.

4.4 Superpermeation

When the diffusion process is the rate determining step for the permeation, the steady-state permeation flux is proportional to the reciprocal thickness of the membrane as Waelbroeck et al. [64, 102, 124] have theoretically shown and mentioned in the chapter 2. The permeation flux at 2100 s was $3.8 \times 10^{16} \text{ m}^{-2}\text{s}^{-1}$ for the sample

2 (see Fig.4.4), which was 4.5 times larger than for the sample 1 at the steady state (see Fig.4.3). The ratio of the thickness of the sample 1 to 2 was 3.3, which suggested the diffusion-limited permeation. One reason for a small difference between the two values of 4.5 and 3.3 is that the permeation in the sample 2 still continued to decrease at that time. Experimental uncertainties such as the amount of the recycled oxygen would have also contributed to the difference.

In the diffusion-limited regime, the deuterium concentration C_{su} near the upstream surface can be obtained from the steady-state permeation flux J_{st} as discussed in 2.1 (see Fig.2.1). Substituting the values of $D = 6.4 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ (see chapter 5), $L = 10^{-4} \text{ m}$ and $J_{st} = 8.4 \times 10^{15} \text{ m}^{-2}\text{s}^{-1}$ into Eq.(2.11), C_{su} was obtained to be $1.3 \times 10^{22} \text{ m}^{-3}$ for the sample 1.

Combining Eqs.(2.7) and (2.8), the particle balance at the steady state is expressed by

$$F = k_u C_{su}^2 + J_{st} \quad (4.1)$$

As the value of C_{su} was obtained above, the recombination coefficient k_u on the upstream can be determined from Eq.(4.1) when the incident flux F is known.

The incident particles to the sample were mainly neutral as mentioned in 4.1. They would be Franck-Condon atoms in the ECH plasma for the discharge cleaning [125], which were produced from the dissociation of hydrogen molecules by the electron bombardment. The value of the neutral flux was difficult to be measured. It was estimated using the following equation [125, 126] derived from the particle balance in the steady-state plasma.

$$\phi_H = 2n_{H_2}n_e\langle\sigma v_e\rangle_{dis}V/A_w \quad , \quad (4.2)$$

where n_{H_2} and n_e are the densities of hydrogen molecules and electrons, respectively, $\langle\sigma v_e\rangle_{dis}$ the rate constant for the dissociation by electrons, V_p the plasma volume (1.7 m^3) and A_w the total surface area of the walls (34 m^2). The density n_{H_2} was

$2.2 \times 10^{17} \text{ m}^{-3}$ when the gas pressure was $9 \times 10^{-4} \text{ Pa}$. The rate constant $\langle \sigma v_e \rangle_{dis}$ is $2.8 \times 10^{-15} \text{ m}^{-3} \text{ s}^{-1}$ [127], assuming the electron temperature to be 4 eV.

When n_e was taken as 10^{17} m^{-3} , which was the largest value in Heliotron E, ϕ_H was obtained to be $5.3 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$ from Eq.(4.2). The incident flux F to the sample was estimated to be $8 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1}$ assuming that the flux was in inverse proportion to the square of the distance from the center of the plasma.

Substituting these values of F , J_{st} and C_{su} into Eq.(4.1), the recombination coefficient k_u on the upstream surface was obtained to be $4.7 \times 10^{-27} \text{ m}^4 \text{ s}^{-1}$. The value agrees with those by Causey et al. [120] in a gas discharge apparatus of a edge-plasma simulator. It is, however, much smaller than those by Yamaguchi et al. [128] in the IDP (ion driven permeation) experiment, where the surface was considered to be clean. This difference would be attributed to the impurities such as oxygen on the upstream surface as suggested in 4.3.

The recombination coefficient k_d on the downstream surface can not be determined experimentally in the diffusion-limited permeation. As oxygen scarcely existed in the downstream system and deuterium continuously diffused from bulk to the downstream surface, the surface was considered to be kept clean. Hence the value of k_d was assumed to be $5.0 \times 10^{-25} \text{ m}^4 \text{ s}^{-1}$, which was the typical value on the clean nickel surface [128] as taken in 3.2.3. Substituting the values of k_d and J_{st} into Eq.(2.8), the deuterium concentration C_{sd} near the downstream surface was obtained to be $1.3 \times 10^{20} \text{ m}^{-3}$. This value was much smaller than C_{su} and consistent with the diffusion-limited permeation.

The condition of $k_u \ll k_d$ in this experiment would be applicable to fusion reactors and have a large effect on evaluating the hydrogen recycling in them. In the IDP experiments using ion guns [56, 57, 60, 105], the upstream surface as well as the downstream one were considered to be kept clean and there have been no signif-

icant differences between the observed recombination coefficients on both surfaces. If k_u was assumed to be the same as k_d under the experimental conditions for the sample 1, the value of J_{st} was estimated to be $7.8 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$ from Eqs.(2.6), (2.7) and (2.8). It was one tenth lower than the observed permeation flux in this experiment.

A ratio between the permeation flux to the incident flux at the steady state, *i. e.* J_{st}/F , is defined as the permeation probability here. The permeation probabilities for the sample 1 and 2 were 0.011 and 0.048, respectively. These values were rather high considering the diffusion-limited permeation. It was because the reemission from the upstream surface was suppressed due to the condition of $k_u \ll k_d$. The permeation with high permeation probability is called the "superpermeation" [54]. This means that the permeation cell with the nickel membranes could monitor the incident neutral particles with a high sensitivity.

4.5 Conclusions

The deuterium PDP in nickel was observed during the ECH-discharge cleaning of Heliotron E. As the results;

1. A large amount of deuterium permeated from the steady-state plasma of Heliotron E.
2. The recombination coefficient k_u on the upstream was much smaller than that on the downstream. This caused the superpermeation in which a ratio of the permeation to the incident flux was rather high.
3. The small value of k_u would be attributed to the recycling of impurities such as oxygen.
4. The deuterium PDP was also observed during the helium discharge, which indicated a significant amount of deuterium being recycled.

5. The permeation flux may be used to monitor the progress of the discharge cleaning.

Chapter 5

In-situ observation of dissolved deuterium

The permeation flux of the PDP was observed in the previous chapters 3 and 4, which is called the permeation method. As the thermal behaviors of hydrogen such as diffusion, permeation and reemission are directly related to the concentration of the dissolved hydrogen, measurements on the hydrogen concentration as well as the permeation flux would bring important information on the thermal behaviors.

In the present work, the in-situ deuterium observation technique was newly developed, in which the NRA (nuclear reaction analysis) and the permeation method were conducted simultaneously. Its advantage is that the deuterium concentration is directly measured. This enables us to determine the diffusion coefficient without influences of the surface impurities as will be discussed in 5.4. Trapping of deuterium could be also observed at elevated temperatures using this method as will be shown in the chapters 6 and 7. An illustration of the in-situ depth profiling is shown in Fig.5.1.

In this chapter, the principle of the NRA and the in-situ deuterium observation method using the NRA are described. Thermal behaviors of deuterium such as diffusion and recombination are discussed based on the experimental results where doses of the probing beam for the NRA are low. The case of higher doses of the probing beam, where traps are produced, will be shown in the next chapter.

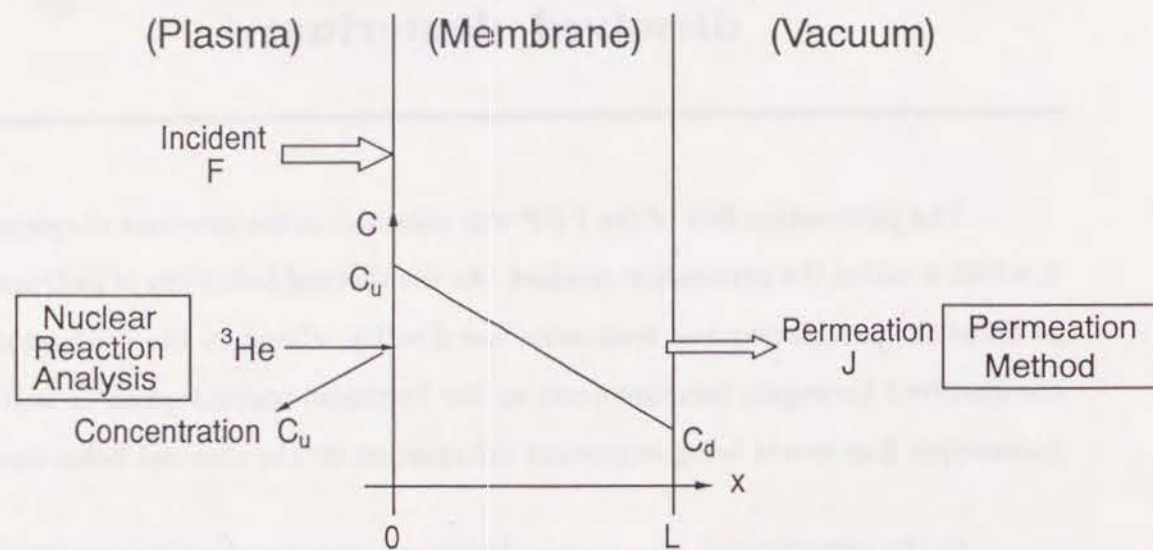


Fig. 5.1. Schematic showing of the in-situ observation of deuterium in metals exposed to deuterium plasmas.

5.1 Nuclear reaction analysis

The NRA with the nuclear reaction $D(^3\text{He},p)^4\text{He}$ [77, 129] observes a depth profile of deuterium in solids. An energy spectrum of protons or alpha particles produced by the reaction is detected when the probing beam of ^3He ions irradiates the solids. A probing depth is larger for detecting protons while a depth resolution is slightly better for detecting alpha particles [78, 81]. As the deuterium concentration in the bulk region is needed in the present work, the proton-detection method [81, 130] is used.

When a ^3He ion with an energy of E_0 enters a metal membrane at an incident angle of η at the surface as shown in Fig.5.2, the ^3He loses its energy as it goes deeper in the metal. A relation between a depth x from the surface and an energy $E_1(x)$ of

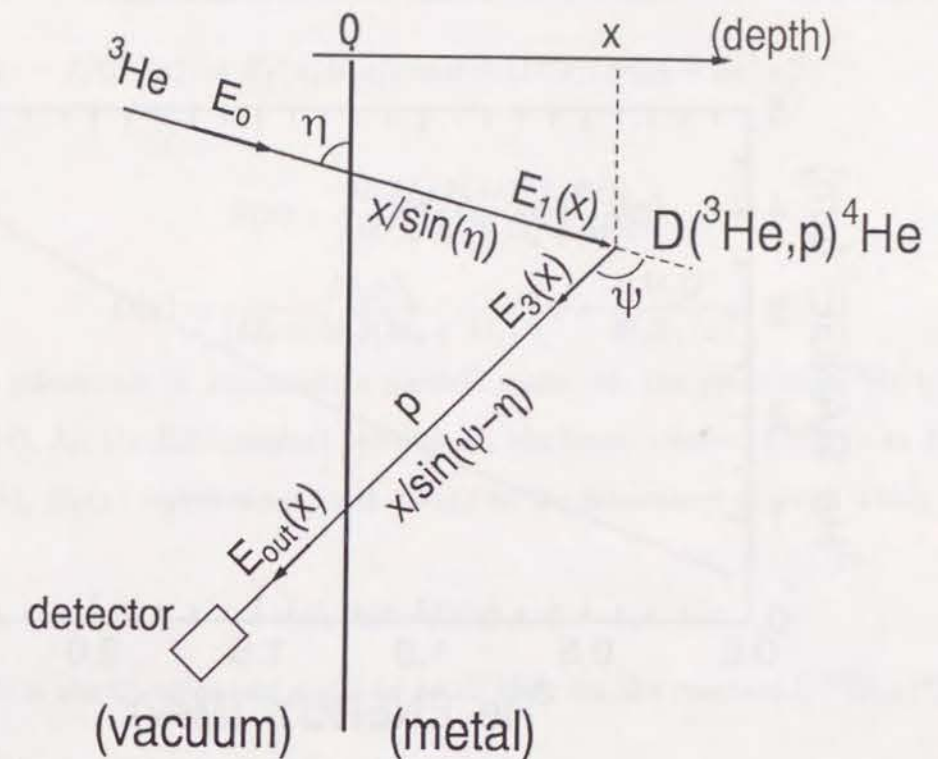


Fig. 5.2. An illustration for the principle of the depth profiling using the nuclear reaction $D(^3\text{He},p)^4\text{He}$.

the ^3He is expressed by

$$\frac{x}{\sin \eta} = R_1(E_0) - R_1(E_1(x)) \quad , \quad (5.1)$$

where a function $R_1(E)$, called the range function, represents the projected mean range of the ^3He with an initial energy of E . When ^3He reacts with deuteron at the depth x and a proton with an energy of $E_3(x)$ is emitted at a scattering angle of ψ , a relation between $E_3(x)$ and an energy $E_{out}(x)$ of the proton arriving at the surface is written by

$$\frac{x}{\sin(\psi - \eta)} = R_3(E_3(x)) - R_3(E_{out}(x)) \quad , \quad (5.2)$$

where $R_3(E)$ is the range function of proton in the metal. Examples of the range

functions in nickel of ^3He and proton [131] are shown in Fig.5.3. The range function increases with the energy and there exists the inverse function.

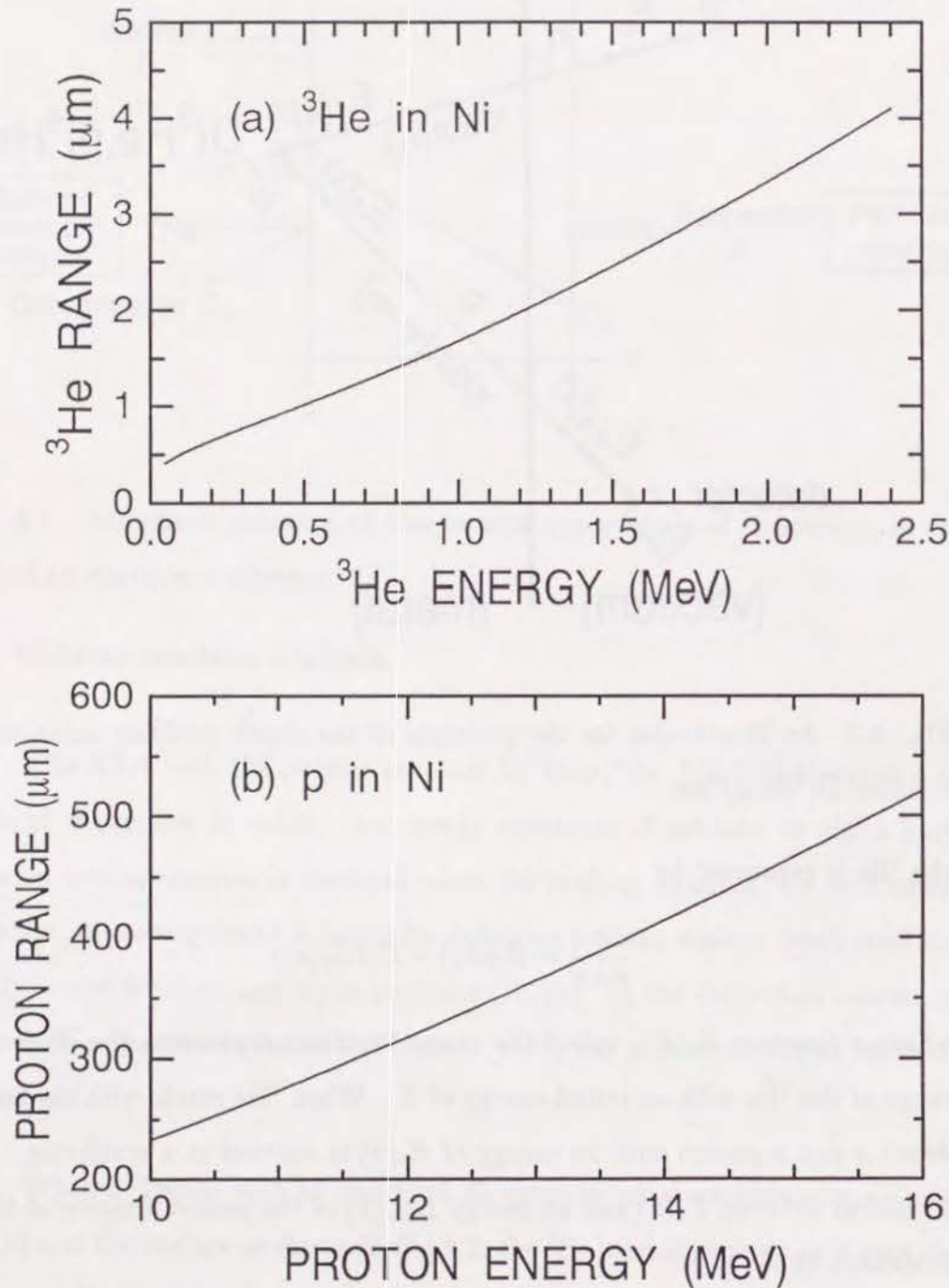


Fig. 5.3. Mean projected ranges of (a) ^3He and (b) proton in nickel[131].

The energy $E_3(x)$ of proton emitted at the scattering angle of ψ at the depth x is defined by $f_\psi(E_1(x))$ and given by the well known Q-equation [132],

$$E_3(x) = f_\psi(E_1(x)) = E_T(x)B(x)[\cos\psi + (D(x)/B(x) - \sin^2\psi)^{1/2}]^2, \quad (5.3)$$

where,

$$B(x) = \frac{M_1 M_3 (E_1(x)/E_T(x))}{(M_1 + M_2)(M_3 + M_4)}, \quad (5.4)$$

$$D(x) = \frac{M_2 M_4}{(M_1 + M_2)(M_3 + M_4)} \left(1 + \frac{M_1 Q}{M_2 E_T(x)} \right). \quad (5.5)$$

Here, a parameter M represents a particle mass: M_1 the projectile (^3He), M_2 the target (d), M_3 the light product (p) and M_4 the heavy product (^4He). In Eqs.(5.4) and (5.5), $E_T(x)$ represents a total energy in the laboratory system, which is given by

$$E_T(x) = E_1(x) + Q, \quad (5.6)$$

where Q is the Q-value and equal to 18.35 MeV for the reaction $\text{D}(^3\text{He}, \text{p})^4\text{He}$.

The emitted proton energies are plotted against the ^3He energies under some values of ψ in Fig.5.4, which are determined from Eqs.(5.3) to (5.6). The figure shows that the dependence of the proton energy on the ^3He energy become larger with increasing ψ . It is clear from Fig.5.4 that the depth resolution converted from the proton energy is better for larger values of ψ .

Combining the above equations, the proton energy $E_{out}(x)$ at the surface is expressed as

$$E_{out}(x) = R_3^{-1} \left[R_3 \left(f_\psi \left\{ R_1^{-1} \left[R_1(E_0) - \frac{x}{\sin\eta} \right] \right\} \right) - \frac{x}{\sin(\psi - \eta)} \right], \quad (5.7)$$

where R_3^{-1} and R_1^{-1} are the inverse functions of R_3 and R_1 , respectively. This equations shows a unique relation between the depth x and $E_{out}(x)$.

A density of deuterium in a small depth width dx at the depth x is expressed by $C(x)dx$, where $C(x)$ is the deuterium concentration. The number $N(E_{out})dE_{out}$

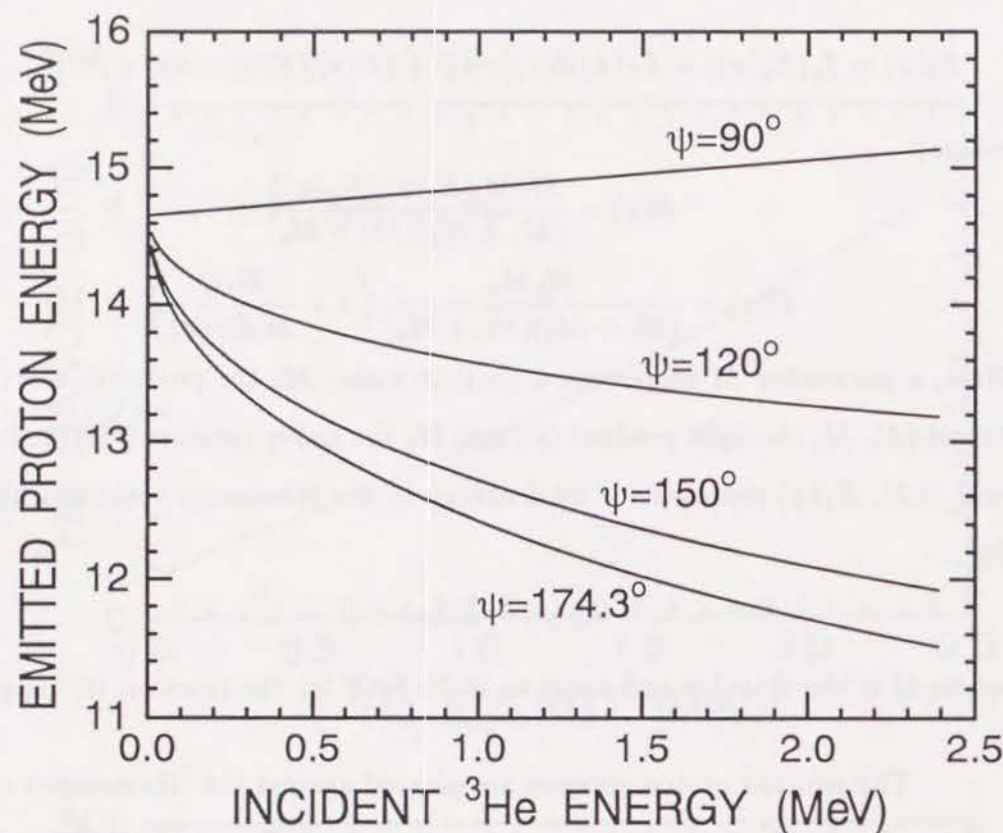


Fig. 5.4. Plots of emitted proton energy versus incident ^3He energy at various laboratory emission angles for the reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$.

of protons which are produced in the width dx and emitted at ψ within a solid angle of Ω is written by

$$N(E_{out})dE_{out} = I \cdot S \cdot C(x)dx \cdot \sigma(\psi) \cdot \Omega \quad , \quad (5.8)$$

where I is the number of ^3He irradiating the membrane per unit area, S the irradiation area of the probing beam and $\sigma(\psi)$ is the differential nuclear cross section for proton at the scattering angle of ψ in the laboratory system. Using Eq.(5.8), one can obtain the deuterium depth profile from the energy spectrum of protons.

Altstetter et al. [133] researched some experimental values of the cross sections

of the nuclear reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$ and gave the numerical expression for the total cross section σ_{tot} of

$$\sigma_{tot} = \frac{5969E^3}{1 - 26.2E^{3.43} + 36.5E^{3.91}} \quad \text{mb} \quad , E \text{ in MeV} \quad , \quad (5.9)$$

where E is the ^3He energy in MeV. The total cross section from Eq.(5.9) is shown in Fig.5.5.

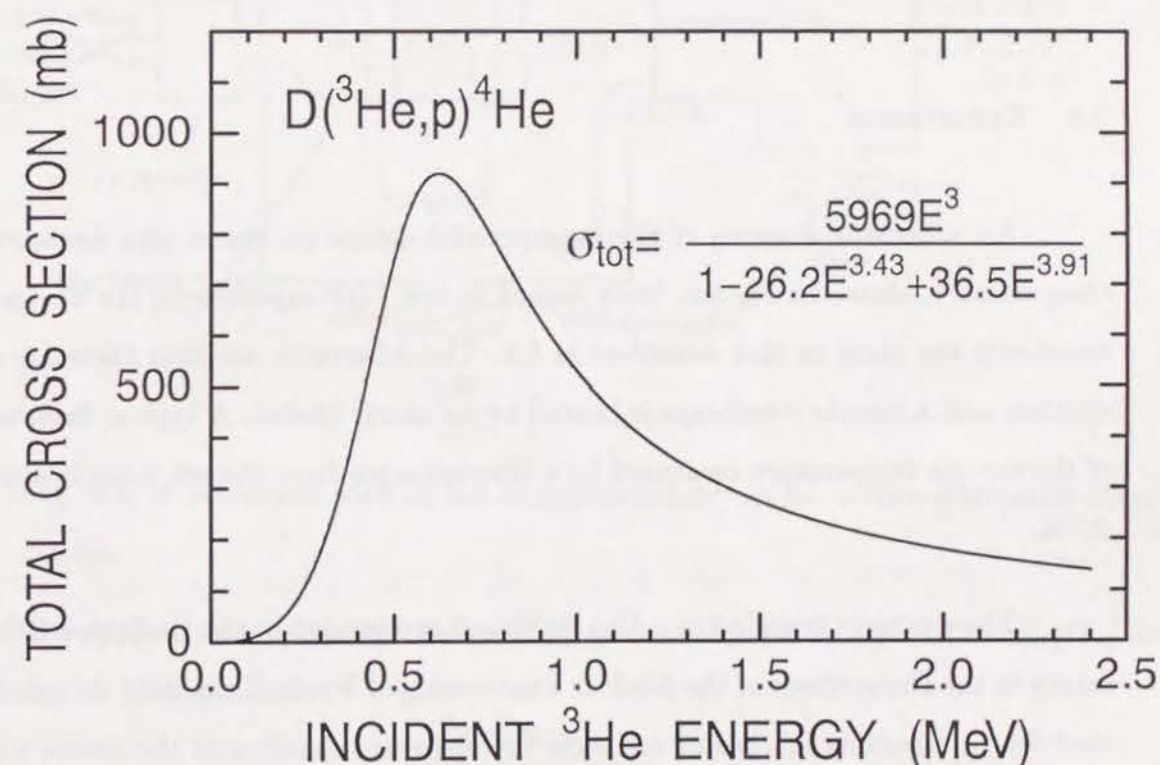


Fig. 5.5. Total cross section (mb) of the nuclear reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$ with the incident ^3He energy (MeV) [133].

As the reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$ is regarded as isotropic in the center-of-mass system [134,135], the differential cross section $\sigma(\psi)$ in the laboratory system is determined by [132]

$$\sigma(\psi) = \frac{\sigma_{tot}}{4\pi} \frac{E_3(x)}{E_T(x)} \left[A(x)C(x) \left(\frac{D(x)}{B(x)} - \sin^2 \psi \right) \right]^{-\frac{1}{2}} \quad , \quad (5.10)$$

where,

$$A(x) = \frac{M_1 M_4 (E_1(x)/E_T(x))}{(M_1 + M_2)(M_3 + M_4)}, \quad (5.11)$$

$$C(x) = \frac{M_2 M_3}{(M_1 + M_2)(M_3 + M_4)} \left(1 + \frac{M_1 Q}{M_2 E_T(x)} \right), \quad (5.12)$$

In Eq.(5.10), $B(x)$ and $D(x)$ are given by Eqs.(5.4) and (5.5), respectively.

Calculations for converting the energy spectrum to the depth profile of deuterium were conducted in the Data Processing Center of Kyoto University.

5.2 Experiment

An schematic drawing of the experimental device for the in-situ deuterium observation is shown in Fig.5.6. With regard to the PDP experiment, the device is essentially the same as that described in 3.2. The differences are that there are no shutters and a sample membrane is heated by an ohmic heater. A typical deviation of the sample temperature measured by a thermocouple from the set value is about ± 1 K.

The device is installed to a Van de Graaff accelerator in the Radiation Laboratory in the Department of the Nuclear Engineering of Kyoto University. A vacuum duct for transporting ion beams connects the upstream chamber of the device with the accelerator. A beam energy of $^3\text{He}^+$ is 1.3 MeV. The ion beam, of which the diameter is adjusted to 4 mm by two slits at 1m apart from each other, irradiates the sample at the incident angle η of 45° .

The protons produced by the reaction $\text{D}(^3\text{He}, \text{p})^4\text{He}$ are detected by a solid state detector of a surface-barrier type (SSD) at the scattering angle ψ of 174.3° . The solid angle Ω of the SSD is 1.08 msr. An aluminum foil with a thickness of $10 \mu\text{m}$ is placed in front of the SSD so as to shield the ^3He ions scattered by the sample.

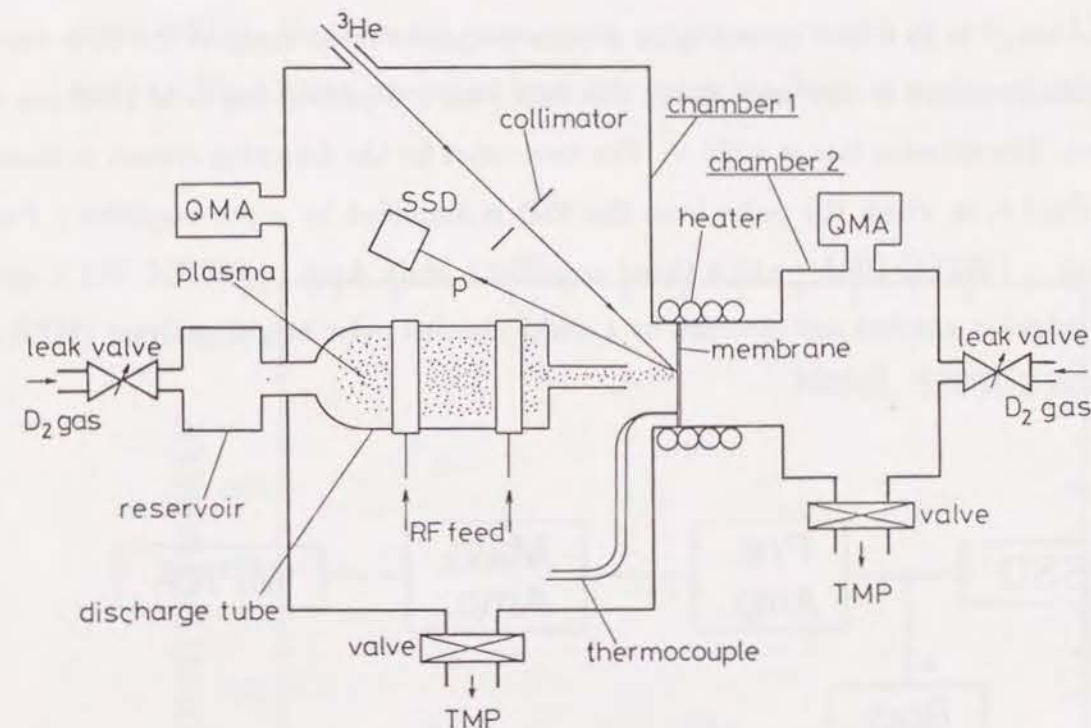


Fig. 5.6. A schematic view of the experimental set up for in-situ deuterium observations.

The typical value of energy losses of the protons by the Al foil is 77 keV [131] for the 14-MeV proton.

There is a pin hole at the center of the aluminum foil so as to monitor a beam current by detecting scattered ^3He ions from the sample. The direct measurement of the $^3\text{He}^+$ beam current is not possible, since electrons as well as deuterium ions come from the rf-plasma to the sample. A relation between the number of the scattered ^3He and the irradiation dose is determined using a Faraday cup, which is placed between the sample and the slits. A beam current is kept less than 200 nA ($7.0 \times 10^{16} \text{ m}^{-2}\text{s}^{-1}$) to prevent an increase in the sample temperature.

From Fig.5.5, ^3He with the energy below 0.2 MeV scarcely reacts with deuterium. When a 0.2-MeV ^3He reacts, an energy of the emitted proton at the scattering angle ψ of 174.3° is 13.6 MeV (see Fig.5.4). As a projected mean range of the 13.6-MeV proton in silicon is $1220\ \mu\text{m}$ [131], the SSD with a depletion depth of $1500\ \mu\text{m}$ is used. The detector bias is +280 V. The electronics for the detecting system is shown in Fig.5.7, in which the pulse from the SSD is amplified by a pre-amplifier (Pre. Amp. : ORTEC 109A) and a linear amplifier (Main Amp. : ORTEC 571), and its height is selected and recorded by a multi-channel pulse height analyzer (MPHA : EG&G 7100).

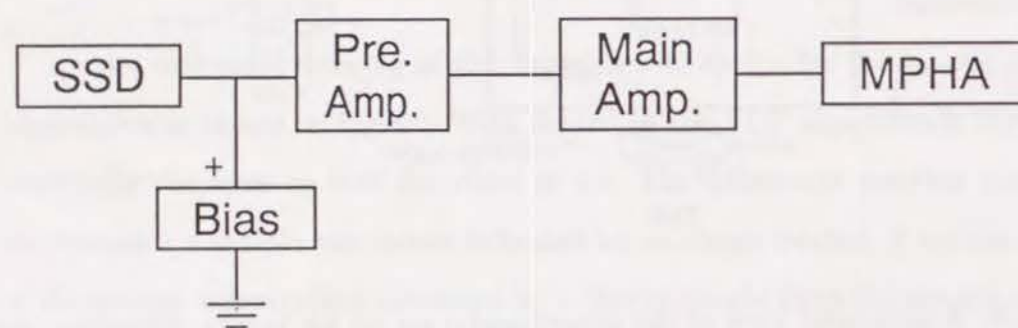


Fig. 5.7. Block diagram of the electronics for the detecting system.

5.3 Depth profiles of deuterium

A nickel membrane with a thickness of 0.1 mm was used for the sample, which was mechanically polished with $0.3\ \mu\text{m}$ alumina finish. The temperature of the sample was kept at 523 K. Deuterium gas with a pressure of 5.3 Pa was fed into the discharge tube and discharged by rf under the plate voltage of 1.4 kV. The deuterium PDP occurred and the permeation flux reached the steady-state value of $1.8 \times 10^{19}\ \text{m}^{-2}\text{s}^{-1}$, which was not changed during the experiments after the steady state was achieved. After that, ^3He irradiated the sample with a dose of $2.0 \times 10^{-3}\ \text{C}$

($7.0 \times 10^{20}\ \text{m}^{-2}$) while the discharge was continued. The energy spectrum of detected protons was shown in Fig.5.8, in which the horizontal axis is represented by channel of the MPHA. One channel corresponds to an energy width of 13.72 keV. A depth profile in Fig.5.9 was converted from the energy spectrum of protons in Fig.5.8.

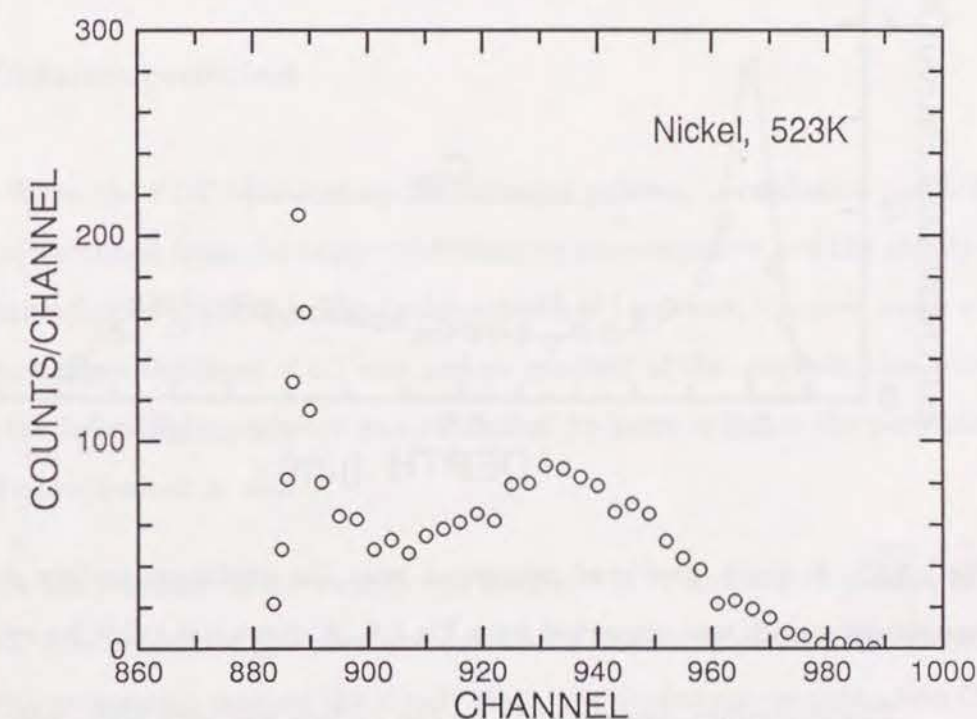


Fig. 5.8. An example of energy spectrum of emitted protons from the nuclear reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$.

A projected mean range of 1.3-MeV ^3He in nickel is $2.1\ \mu\text{m}$ [131]. As the beam irradiated at the angle of 45° , the corresponding mean depth was $2.1\ \mu\text{m} \times \cos(45^\circ) \approx 1.5\ \mu\text{m}$. A probing depth was limited around $1.0\ \mu\text{m}$ because of small cross sections for low energy ^3He particles as shown in Fig.5.5. An energy resolution was not taken into account in the conversion and the concentration on the surface extended to $\pm 0.2\ \mu\text{m}$ depth in Fig.5.9.

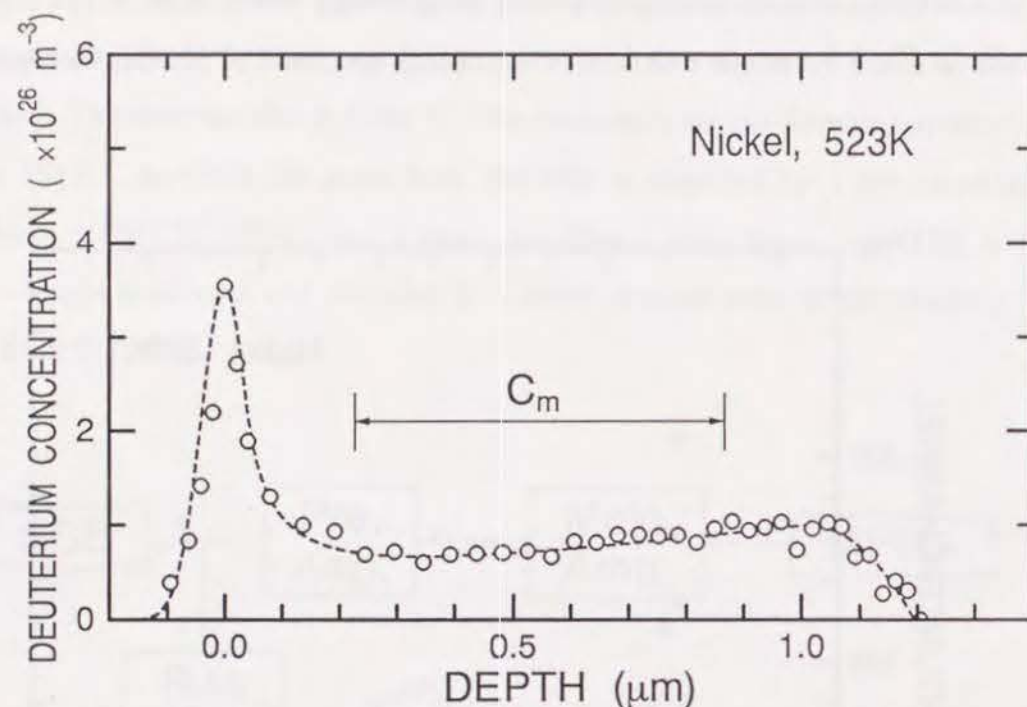


Fig. 5.9. A depth profile of deuterium near the upstream surface during PDP experiment, which was converted from Fig.5.8. A curve is a guide for eyes.

The deuterium concentration on the surface was very high, which would be due to a large amount of deuterium absorbed on the surface. Impurities such as oxygen on the surface was also responsible as will be discussed in 5.4. In this case of the high concentration on the surface, the recombination rate of deuterium was considered to be still proportional to the square of the concentration of deuterium dissolved just beneath the surface as shown by Wampler et al. [73,136].

A broad peak around a 930 channel in Fig.5.8 corresponded to the peak of the cross section (see Fig.5.5). Hence it was not seen in the depth profile in Fig.5.9 and deuterium in the bulk was found to uniformly distribute. A slight increase in the concentration with the depth was attributed to the traps produced by the probing

beam, which will be discussed in the chapters of 6 and 7.

The observed deuterium concentration C_m was defined by the average value over the depth of 0.2 to 0.8 μm , which will be used in this and the next chapters. It represents the deuterium concentration just beneath the upstream surface in the bulk.

5.4 Diffusion coefficient

When the PDP is limited by the diffusion process, the diffusion coefficient D can be determined from the observed deuterium concentration and the steady-state permeation flux by Eq.(2.11). The probing depth of 1 μm was, however, much smaller than the sample thickness of 0.1 mm and no gradient of the concentration was seen. Hence the following experiment was conducted to know whether the permeation is the diffusion-limited or not.

A temperature of the sample was held at 523 K and the rf-plasma was discharged. The deuterium gas pressure was 5.3 Pa and the plate voltage was 0.7 kV. After the permeation reached the steady state, the deuterium concentration C_m was observed by the NRA. The permeation flux was subsequently changed by increasing the pressure of the deuterium gas or the rf power, and C_m was observed again at the new steady state. This procedure was repeated several times. The total dose of ^3He was $4 \times 10^{20} \text{ m}^{-2}$. The permeation flux J_{st} was plotted against C_m as shown in Fig.5.10.

This figure shows a linear relation between J_{st} and C_m . As there would be no traps under low doses of ^3He , C_m was considered to be equal to the concentration of deuterium C_{su} dissolved just beneath the upstream surface. The permeation was found to be limited by the diffusion process. This was consistent with the result of

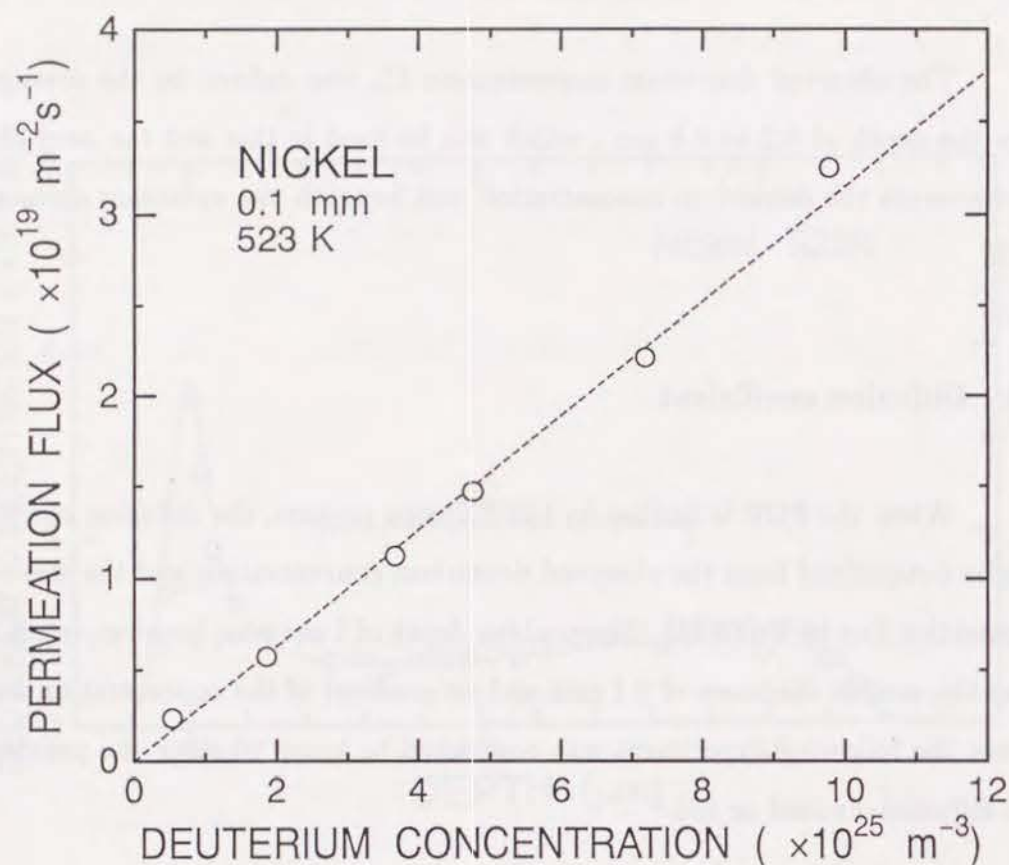


Fig. 5.10. A linear relation between observed deuterium concentrations just beneath the upstream surface and permeation fluxes at low doses of ^3He .

the PDP experiments at the non-steady state in 3.2.

The values of J_{st} and C_m at the steady state were observed at the temperatures of 455, 483, 523 and 568 K. A non-irradiated sample was used for each measurement and the ^3He dose was kept less than $1 \times 10^{20} \text{ m}^{-2}$ to minimize effects of the traps. The experimental conditions were the same, in which the sample thickness was 0.1 mm, the gas pressure 5.3 Pa and the plate voltage 0.7 kV. The diffusion coefficients, which were determined from J_{st} and C_m by Eq.(2.11) are shown by closed circles in Fig.5.11.

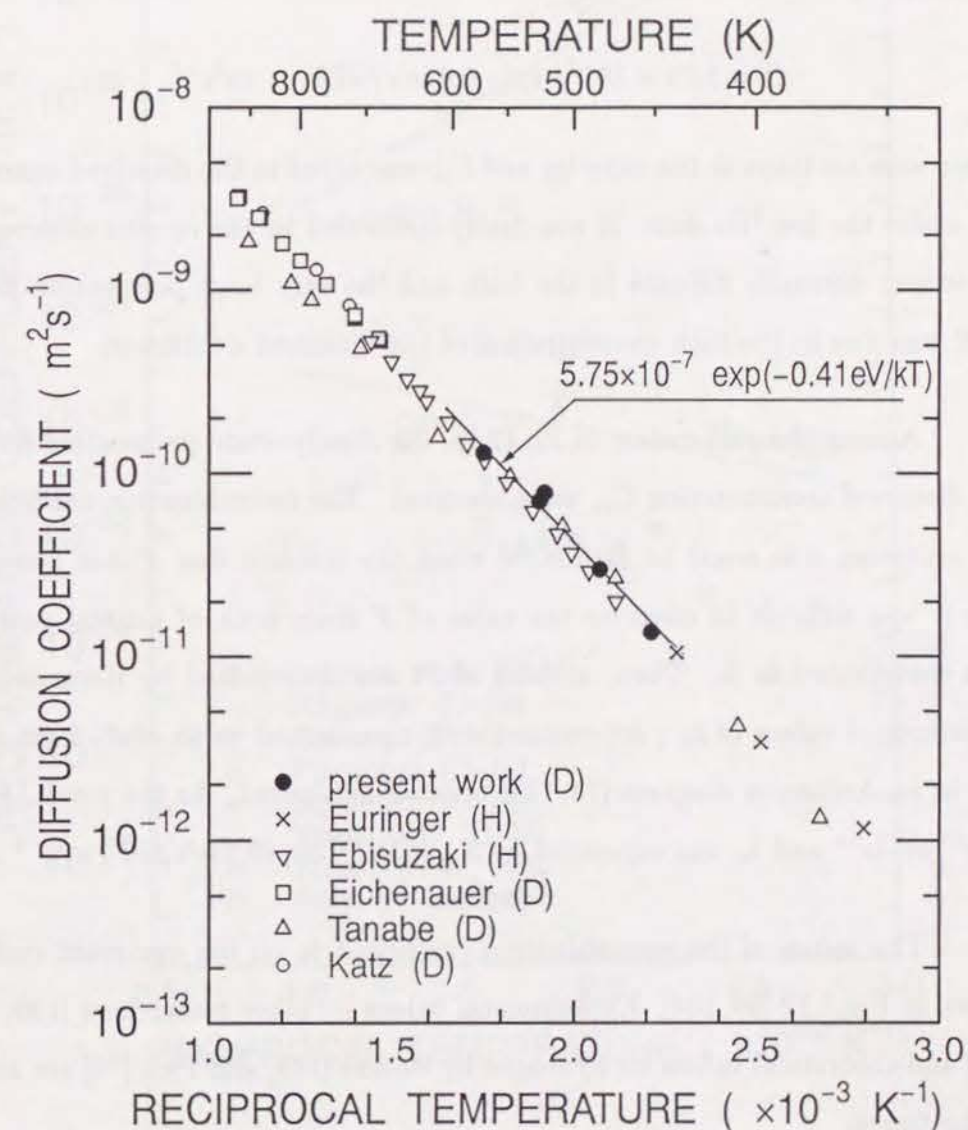


Fig. 5.11. Diffusion coefficients of hydrogen isotopes in nickel. Closed circles represent experimental results in the present work.

The data in the figure are on a straight line in an Arrhenius diagram and agree well with those of other works [20, 28, 137–139] by means of the permeation method. This indicated that the permeation was limited by the diffusion process between the temperatures of 455 and 568 K. By the data fitting, the diffusion coefficient D was expressed by

$$D = 5.75 \times 10^{-7} \exp(-0.41\text{eV}/kT) \quad \text{m}^2\text{s}^{-1} \quad (5.13)$$

There were no traps in the samples and C_m was equal to the dissolved concentration C_{su} under the low ^3He dose. It was firstly confirmed by the in-situ observation that deuterium normally diffused in the bulk and the very large permeation flux of the PDP was due to the high concentration of the dissolved deuterium.

Among the parameters in Eq.(2.7), the steady-state permeation flux J_{st} and the dissolved concentration C_{su} were observed. The recombination coefficient k_u on the upstream side could be estimated when the incident flux F was known. However it was difficult to measure the value of F since both of neutral particles and ions contributed to it. Then, a value of F was determined by iteration in which deviations of values of k_u , determined with an assumed value of F , from a straight line in an Arrhenius diagram [73, 136] became minimized. As the result, F was $4.3 \times 10^{19} \text{ m}^{-2}\text{s}^{-1}$ and k_u was expressed by $3.1 \times 10^{-33} \exp(0.24\text{eV}/kT) \text{ m}^4\text{s}^{-1}$.

The values of the recombination coefficient k_u on the upstream surface were shown in Fig.5.12 [69, 104]. Experimental values by other researchers [120, 128, 140–144] and theoretical values for hydrogen by Baskes [145] and Pick [70] are also shown in the figure.

The values of k_u rather deviate from the straight line in Fig.5.12 due to experimental uncertainties, which was probably the inconstant amounts of the impurities, but not the incident flux.

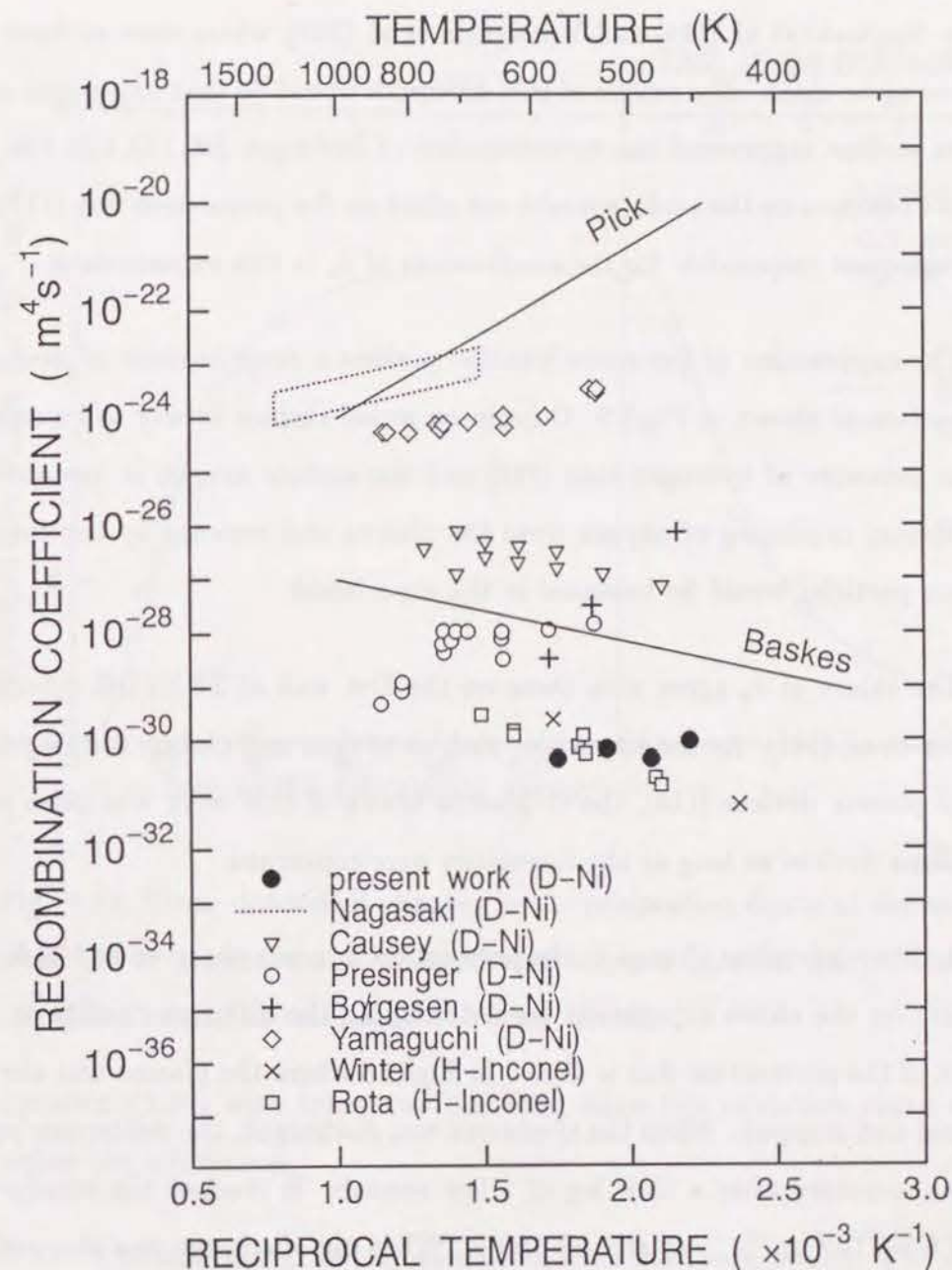


Fig. 5.12. An Arrhenius diagram of recombination coefficients of hydrogen isotopes on nickel and its alloys determined experimentally (symbols) and theoretically (lines).

The values in the present work are smaller than those from the IDP experiments by Nagasaki et al. [144] and Yamaguchi et al. [128], where their surfaces were considered to be clean. The reason of this difference would be that impurities on the upstream surface suppressed the recombination of hydrogen [95,122,123,136,146]. As sulfur or carbon on the surface would not affect on the permeation flux [119,120], oxygen was most responsible for the small values of k_u in this experiment.

The suppression of the recombination yielded a large amount of deuterium on the surface as shown in Fig.5.9. Oxygen on nickel surface is easy to be removed under an exposure of hydrogen ions [122] and the surface oxygen is unstable if it exists. Hence, impinging of oxygen from the plasma and removal by the energetic deuterium particles would be balanced in the experiment.

The values of k_u agree with those on the first wall of TEXTOR determined by Winter et al. [141]. As the impurities such as oxygen and carbon are recycled in the large plasma devices [118], the rf-plasma device of this work was close to the large plasma devices as long as the impurities were concerned.

A time-dependent change in the permeation flux was observed at 523 K prior to conducting the above experiment for determining the diffusion coefficient. The evolution of the permeation flux is shown in Fig.5.13 where the plasma was abruptly discharged and stopped. When the rf-plasma was discharged, the deuterium permeation flux increased after a time lag of a few seconds. It reached the steady-state value of $6.0 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$ at around 100 s. When the discharge was stopped, the permeation flux rapidly decreased toward zero.

The evolution curve in Fig.5.13 was estimated by the numerical calculation described in the chapter 2. The permeation flux was obtained from Eq.(2.2), in which the dissolved deuterium concentration was numerically calculated using the diffusion equation (2.1) under the boundary conditions of Eqs.(2.3) and (2.4). The diffusion

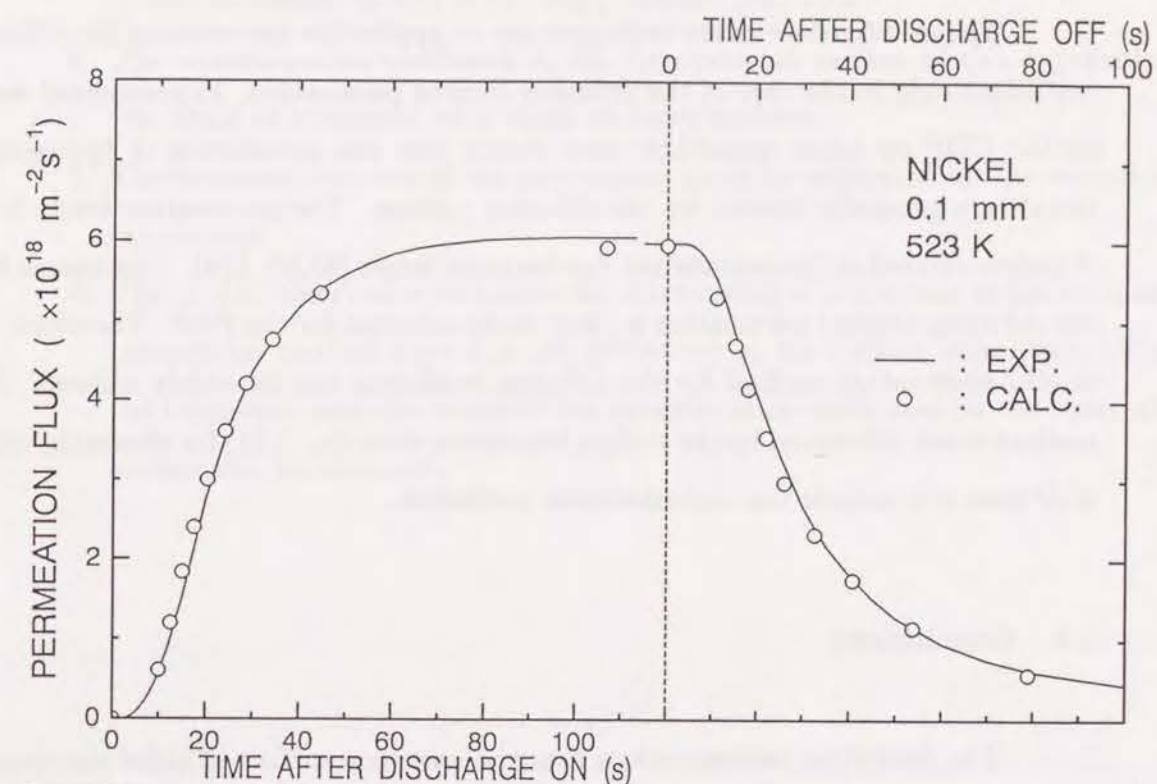


Fig. 5.13. Time-dependent changes in the permeation fluxes of deuterium in nickel after the rf plasma was discharged and stopped (a solid line). The numerically calculated results are also shown as open circles.

equation (2.20) with traps was not used since this evolution curve was observed before the irradiation.

The values of D and k_u were taken from the above results. The recombination coefficient k_d on the downstream does not affect the permeation flux in the diffusion-limited permeation, so a value of $3 \times 10^{-28} \text{ m}^4\text{s}^{-1}$ was used to assure the diffusion-limited permeation.

The calculated results shown in Fig.5.13 agreed well with the experimental curve. This confirmed that the parameters of D , k_u and F obtained from the steady-

state experiment were valid.

The in-situ observation technique can be applied for determining the diffusion coefficient only in the case of the diffusion-limited permeation. Experimental works on the GDP by other researchers have shown that the permeation of hydrogen in metals are generally limited by the diffusion process. The permeation tends to be diffusion-limited as the permeation flux becomes larger [63, 65, 124]. This means that the diffusion-limited permeation is likely to be achieved for the PDP. Therefore, the in-situ observation method for the diffusion coefficient can be widely utilized. This method is not influenced by the surface impurities since Eq.(2.11) for obtaining values of D does not include the recombination coefficient.

5.5 Conclusions

The deuterium concentrations near the upstream surface of nickel membranes were observed using the NRA, where the membranes were continuously exposed to the deuterium plasma. As the results;

1. It was first confirmed that the high concentration of dissolved deuterium yielded the large permeation flux of the PDP.
2. Observed deuterium below 1- μm depth uniformly distributed while the concentration of absorbed deuterium at the surface was very high. The latter was attributed to the surface impurities such as oxygen.
3. At low doses of the probing beam, the observed deuterium concentration was equal to the dissolved one. There were no effects of traps.
4. The linear relation between the permeation flux of the PDP and the observed deuterium concentration indicated that the permeation was diffusion-limited under our experimental conditions.

5. The diffusion coefficient D could be directly obtained by the present method. It was expressed by $5.75 \times 10^{-7} \exp(-0.41\text{eV}/kT) \text{ m}^2\text{s}^{-1}$.
6. The recombination coefficient k_u on the upstream surface of this experiment was small as compared with those on clean surfaces.
7. The transient behavior of the permeation could be estimated by the numerical calculation.
8. The in-situ observation technique for determining D is superior to the ordinary permeation method since it is not influenced by the surface impurities. Using the technique, also the values of the recombination coefficient on the upstream surface can be obtained.

Chapter 6

Deuterium trapping

In this chapter, the relation between the density of the traps and the concentration of the trapped deuterium, and effects of the traps on the permeation of the PDP will be discussed. The experimental procedure and device is the same as in the previous chapter, but the dose of the irradiation by the ^3He beam is much larger so that the produced radiation damage may affect the deuterium distribution via generating the traps.

6.1 Production of traps

The observed deuterium concentration, defined in the previous chapter, is the sum of the dissolved concentration C_{su} and the trapped one C_{tu} at the steady state when traps are present. It represents the deuterium inventory near the upstream surface and is expressed by

$$C_m = C_{su} + C_{tu} \quad . \quad (6.1)$$

As C_{su} is estimated from the permeation flux in Eq.(2.11) in the diffusion-limited permeation, a value of C_{tu} can be determined by subtracting C_{su} from C_m .

In the experiment, a 0.1-mm thick nickel sample was heated and exposed to the deuterium rf-plasma. After the permeation of the deuterium PDP reached the steady-state, the beam of 1.3-MeV ^3He was continued to irradiate the sample. The temperature and the condition of the plasma were kept constant. As the result, the observed concentration C_m increased with the ^3He dose, while no changes in the permeation flux were monitored. This indicated that the trap density increased

due to the ^3He irradiation. The evolutions of the concentration C_{tu} of the trapped deuterium against the ^3He dose at some temperatures are shown in Fig.6.1. A non-irradiated sample was used for each measurement.

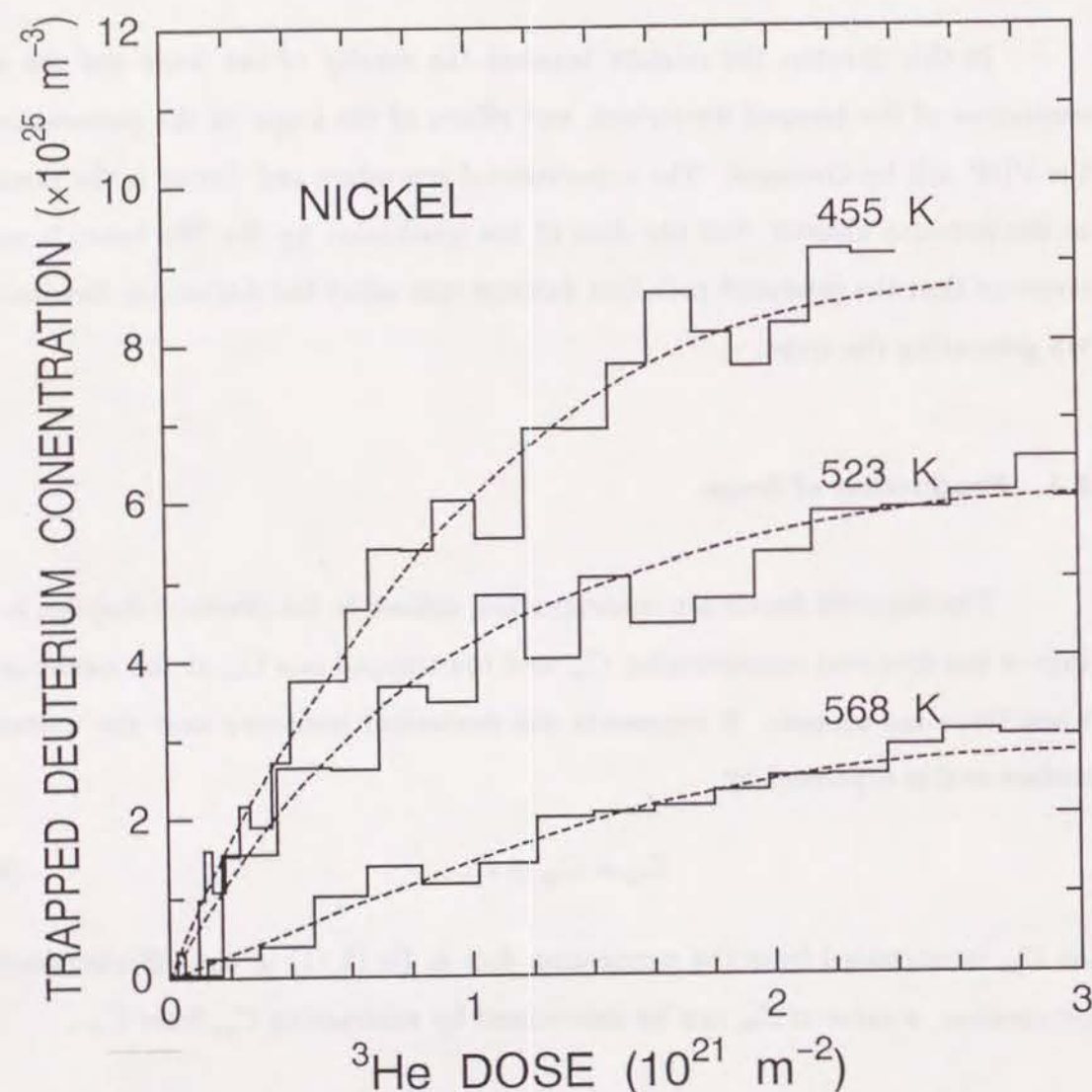


Fig. 6.1. Evolutions of trapped deuterium concentrations with doses of ^3He under steady-state permeation of the PDP. Dashed lines are guides of eyes.

At low doses of ^3He , C_{tu} increased almost linearly with the dose while it tended to be saturated at higher doses. This suggested that the disappearance and

the production of the traps were in equilibrium.

The concentration C_{su} of dissolved deuterium at 523 K was $0.8 \times 10^{25} \text{ m}^{-3}$, which was obtained from Eq.(2.11). The observed concentration C_m at the dose of $2.5 \times 10^{21} \text{ m}^{-2}$ was $6.8 \times 10^{25} \text{ m}^{-3}$. The trapped concentration C_{tu} was then $6.0 \times 10^{25} \text{ m}^{-3}$ as shown in the figure. This value was much larger than C_{su} , and it was found that the observed concentration, i. e. the inventory, was nearly equal to the trapped deuterium concentration. Effects of the traps on the inventory in the plasma-facing materials will be discussed in 6.4.

6.2 Trap density

A sample was held at a temperature of 523 K and irradiated by 1.3-MeV ^3He up to $3 \times 10^{21} \text{ m}^{-2}$ under the steady state of permeation. The observed concentration reached almost saturated value at the dose of $3 \times 10^{21} \text{ m}^{-2}$ as shown in Fig.6.1. The discharge and the feed of deuterium gas were subsequently stopped but the irradiation continued to obtain depth profiles. The observed concentration C_m slowly decreased with time as shown in Fig.6.2.

The decrease of C_m with time shown in Fig.6.2 was reproduced by the calculation, in which the coupled differential equations (2.20) and (2.31) were numerically solved under the boundary conditions of Eqs.(2.3) and (2.4). In the calculation, the trap was assumed to distribute uniformly up to the depth corresponding to the mean projected range of the incident ^3He ion. The trap density was considered to be independent of time since the value of C_m was already saturated when the discharge was stopped. The incident flux F , the recombination coefficients k_u and k_d and the diffusion coefficient D were taken from the section 5.4.

The parameter f in Eq.(2.31) is a function of the trap density C_o . It is

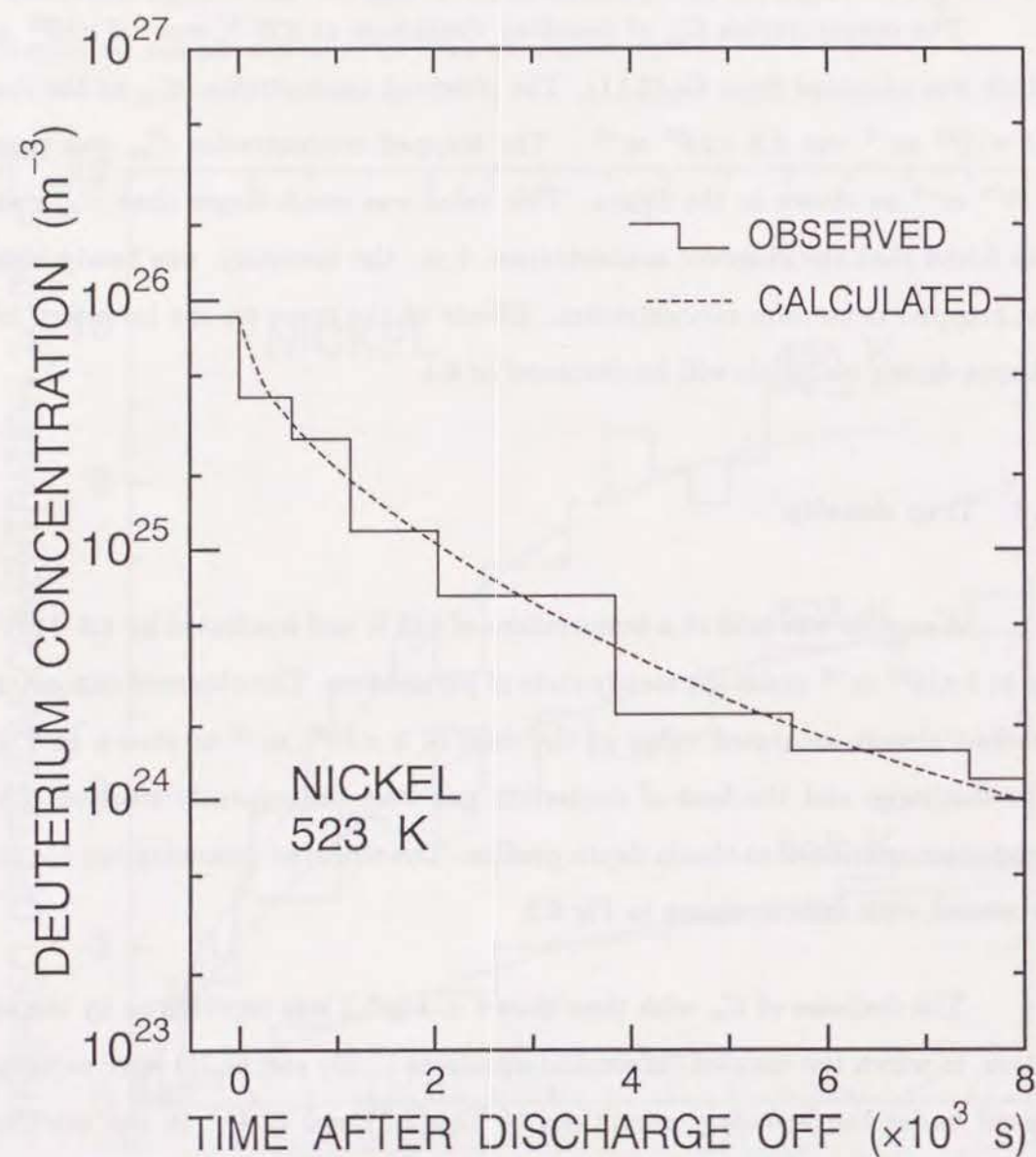


Fig. 6.2. Time-dependent decrease of observed deuterium concentration after discharge was stopped. A solid line and a dashed line represent the experimental and the calculated results, respectively.

expressed by

$$f = \frac{C_{su}(C_o - C_{tu})}{NC_{tu}}, \quad (6.2)$$

which is derived from Eq.(2.33) at the steady state. As all the parameters in Eq.(6.2) are time-independent, the relation between f and C_o is determined uniquely, where the values of C_{su} and C_{tu} are obtained from the measurement just before the discharge was stopped. Substituting Eq.(6.2) into Eq.(2.31), a fitting parameter is only C_o . Hence, the value of C_o was determined so that the calculated result reproduced the experimental data in Fig.6.2, where C_{su} and C_{tu} were used for the initial values at $t = 0$. The result is shown in the same figure. The trap density C_o was found to be $8.3 \times 10^{25} \text{ m}^{-3}$ (9.0×10^{-4} atom fraction). As the concentration of trapped deuterium was $7.7 \times 10^{25} \text{ m}^{-3}$, most traps were occupied by deuterium even at the elevated temperature of 523 K.

Similar experiment were performed at different temperatures of 455, 483 and 568 K. The other experimental conditions were the same and a new sample was used for each experiment. As the results, the time-dependent changes in the observed concentration were all reproduced by calculation with the fitting parameter C_o . It was found that C_o tended to increase with decreasing temperature. For instance, values of C_o were $4.5 \times 10^{25} \text{ m}^{-3}$ (4.9×10^{-4} atom fraction) at 568 K and $1.2 \times 10^{26} \text{ m}^{-3}$ (1.3×10^{-3} atom fraction) at 455 K, respectively. This was reasonable considering that the traps disappeared by some thermally activated processes such as the diffusion of defects.

The values of f were determined from C_o in Eq.(6.2), for example, $f = 4.7 \times 10^{-6}$ at 568 K. The plot of f on an Arrhenius diagram gave the trapping energy of 0.14 eV.

The average energy transferred to target atoms per unit length by incident ions is generally largest near the projected range of the ion. The concentration of

radiation induced defects would be higher near the end of the projected range of ^3He than near the surface. However, the deuterium concentration near the end of the projected range could not be observed due to the small cross sections of ^3He . Hence, the trap density C_o obtained above is a mean value over the surface to the $0.8\text{ }\mu\text{m}$ depth, in which the density of the defects was relatively low.

The traps were assumed to distribute uniformly from the surface to the $1.5\text{ }\mu\text{m}$ depth (the projected range $\times \cos 45^\circ$) in the calculation. In fact, the trap density would be higher near the end of the projected range. Effects of this on the calculated results will be discussed. A time where the permeation flux at 523 K decreased to 10% after the stop of the discharge was 80 s (see Fig.5.13). The dissolved deuterium would be almost desorbed from the sample in this time. The observed deuterium concentration C_m decreased to 10% of the original value at over 2000 s after the stop of the discharge as shown in Fig.6.2. These results indicated that the detrapping process of trapped deuterium was dominant and the trapping of the dissolved deuterium was rare after the discharge was stopped. Hence the time-dependent change in the deuterium concentration around the projected range would be the same as in the observed depth region.

6.3 Effect of traps on PDP

The permeation flux at the steady state is not affected by the traps, which is shown by Eq.(2.2). An influence of the traps on the permeation at the non-steady state will be discussed. After the measurement of the permeation flux shown in Fig.5.13, the plasma was discharged again and ^3He irradiated the sample up to $3 \times 10^{21}\text{ m}^{-2}$. The steady-state permeation flux was not changed by the ^3He irradiation. The discharge was subsequently stopped and the time-dependent change in the permeation flux was observed again, which is shown in a dashed line in Fig.6.3.

The permeation flux observed before the irradiation is also shown as a solid line in the figure.

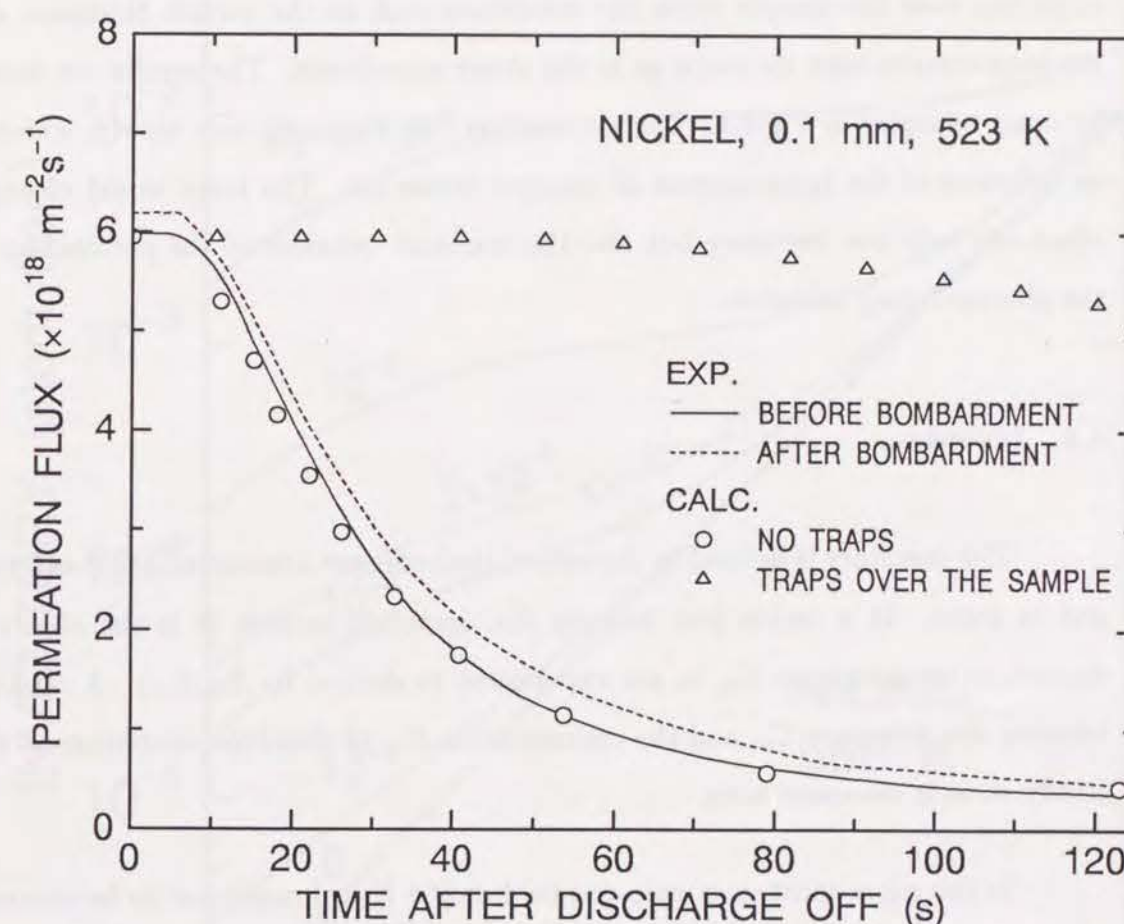


Fig. 6.3. Influences of traps on the permeation flux after the discharge was stopped. No changes are seen between the two experimental curves obtained before and after the bombardment of ^3He ions. The calculated results (triangles) predict a very slow decrease when the traps are present in all over the sample.

The two experimental curves agreed well with each other within experimental errors. This indicated that the traps caused little effects on the permeation rate at the non-steady state in this experiment. The reason was that the traps only existed in a shallow region where the incident ion reached.

In the plasma-facing materials of fusion reactors, 14-MeV neutrons from the D-T reactions penetrate deep into the materials and would produce the radiation damages. So another calculation was conducted assuming that the traps distributed uniformly over the sample while the conditions such as the sample thickness and the temperature were the same as in the above experiment. The results are shown by open triangles in Fig.6.3. The permeation flux decreases very slowly, which is an influence of the large amount of trapped deuterium. The traps would strongly affect not only the inventory but also the transient behavior of the permeation in the plasma-facing materials.

6.4 Inventory

The inventory is defined by the sum of the hydrogen concentrations in solution and in traps. In a region just beneath the upstream surface, it is the observed deuterium concentration C_m in our experiment as defined by Eq.(6.1). A relation between the inventory C_m and the concentration C_{su} of dissolved deuterium at the steady state is discussed here.

In the experiment, a sample was held at 568 K and continued to be exposed to the deuterium plasma. The beam of 1.3-MeV ^3He irradiated the sample simultaneously. After the observed concentration saturated at the dose of $5 \times 10^{21} \text{ m}^{-2}$, the permeation flux and the deuterium concentration were observed. The permeation flux was subsequently changed by changing the rf power supplied to the plasma and the pressure of deuterium gas. The value of C_m was observed again at the new steady state. This procedure was repeated three times. Open circles in Fig.6.4 show the plot of the inventory C_m against the dissolved concentration C_{su} determined from the permeation flux. Both C_m and C_{su} are represented by the atom fraction to nickel.

Combining Eqs.(6.2) and (6.1) to eliminate the trapped concentration C_{tu} ,

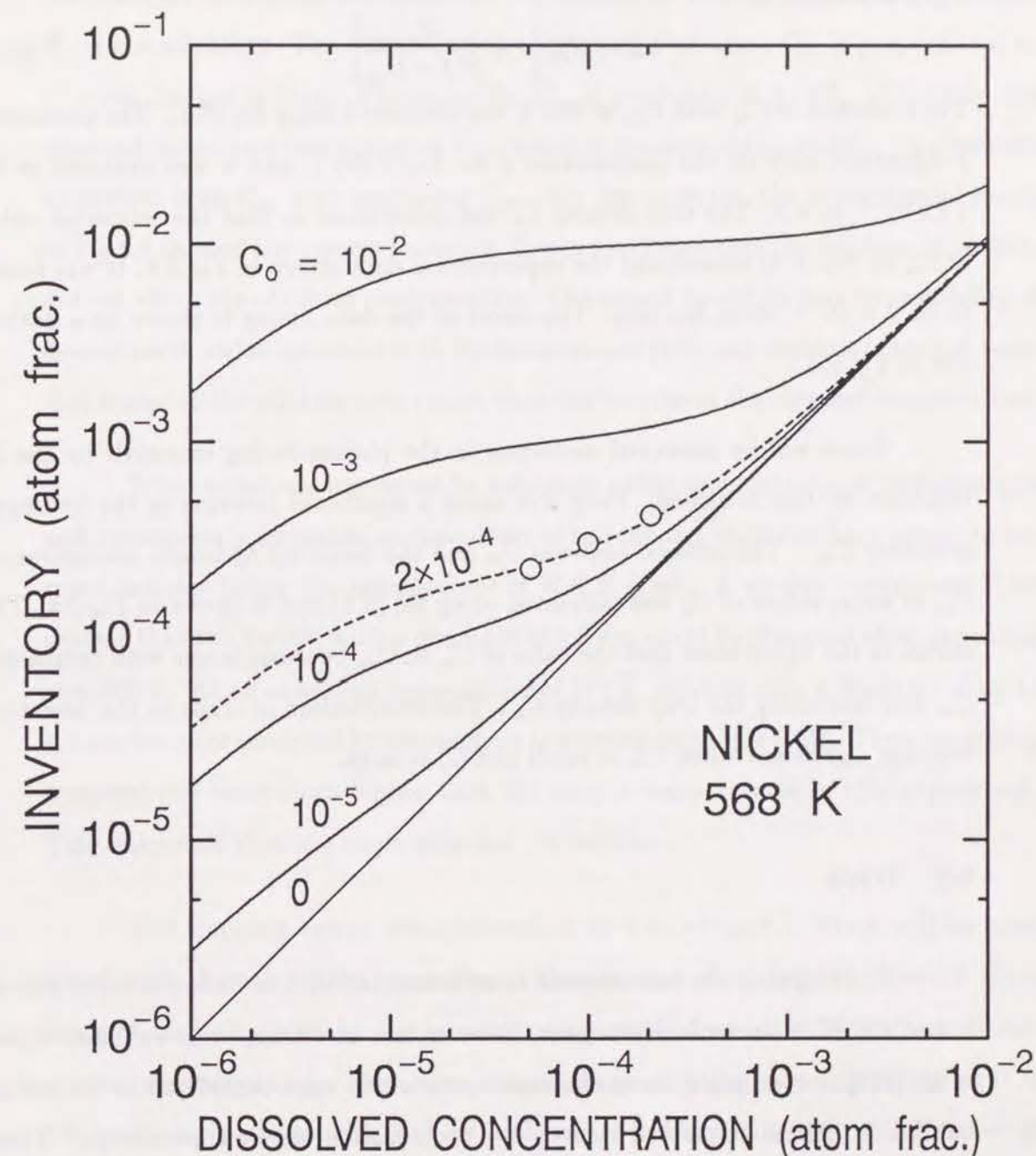


Fig. 6.4. Relations between inventory C_m and dissolved concentration C_{su} at 568 K under some values of trap density C_0 in nickel. The inventory is the sum of the trapped and the dissolved concentrations. All values are represented in atom fractions. The experimental data are shown as open circles.

C_m is expressed by

$$C_m = C_{su} \left[1 + \frac{C_o}{Nf + C_{su}} \right] \quad (6.3)$$

The evolution of C_m with C_{su} at 568 K was evaluated using Eq.(6.3). The parameter f depended only on the temperature (see Eq.(2.26)), and it was obtained to be 4.7×10^{-6} in 6.2. The trap density C_o was determined so that the estimated value of C_m by Eq.(6.3) reproduced the experimental data shown in Fig.6.4. It was found to be 2×10^{-4} atom fraction. The result of the data fitting is shown as a dashed line in Fig.6.4.

Traps will be produced uniformly in the plasma-facing materials by the irradiation by fast neutrons. They will cause a significant increase in the hydrogen inventory C_m . The relation between C_m and the dissolved hydrogen concentration C_{su} at some values of C_o was estimated using Eq.(6.3) and is shown in Fig.6.4. The curves in the figure show that the ratio of C_m to C_{su} becomes larger with decreasing C_{su} and increasing the trap density C_o . The contribution of traps to the inventory becomes significant when C_{su} is small and C_o is large.

6.5 Traps

The trapping site was assumed to be associated with radiation induced defects in the above discussions. Hydrogens, however, are also trapped in bubbles. Myers et al. [147], for example, have observed spots which were considered to be helium bubbles in helium-implanted iron by the transmission electron microscopy. These bubbles may have existed near the end of the projected range of the bombarding ^3He ion in our experiment. The bubble is defined here by such a space where deuterium are trapped as D_2 gas.

In the diffusion-limited permeation, Sieverts' law (see Eq.(1.2)) gives a linear relation between the square root of the deuterium-gas pressure P in a bubble and

the dissolved deuterium concentration C_{su} around it. That is, $C_{su} = K\sqrt{P}$, where K is the solubility. The concentration of trapped deuterium C_{tu} is proportional to P when the gas is ideal. Consequently, C_{tu} is proportional to C_{su}^2 . Therefore the observed deuterium concentration C_m , which is the sum of C_{su} and C_{tu} , is expected to deviate from C_{su} with increasing C_{su} . On the contrary, the experimental result in Fig.6.4 showed the inverse tendency. It was concluded that the bubbles, if existed, did not affect the observed concentration. The reason would be that the solubility of deuterium in nickel increased with the temperature [137] and deuterium tended to be distributed in the solution sites rather than the bubbles at the elevated temperatures.

When nickel was implanted by helium up to the concentration of 1000 atm. ppm and subsequently annealed, no complexes of helium and vacancies have grown to become bubbles below the temperature of 650 K [148]. A similar experiment [149] showed that the bubble with a diameter of 0.8 nm could be observed after annealing over 900 K. At an annealing temperature of 773 K, bubbles with a diameter of up to 1.2 nm were not observed by the neutron scattering technique [150]. These annealing temperatures were much higher than the sample temperatures in this experiment. This supported that the traps were not the bubbles.

The trapping energy was obtained to be 0.14 eV in 6.2, which will be compared with those by other researchers. Besenbacher et al. [93, 94] observed three kinds of traps in nickel by the ion channeling method and the TDS (thermal desorption spectroscopy). They were monovacancy with the trapping energy of 0.24 eV, multiple vacancies with 0.43 eV and helium bubbles with 0.55 eV. Nørskov et al. [151] have derived trapping energies theoretically as 0.17 eV for the interstitial associated trap, 0.43 eV for the multiple vacancies and 0.57 eV for the helium bubble. Yasukawa et al. [152] showed that interstitial loops in nickel trapped deuterium at elevated temperatures and the loop density tended to be saturated with time, or electron dose under electron irradiations. This was similar to the dose-dependence

changes in the trapped deuterium concentration as shown in Fig.6.1. From above discussions, the observed trap would be associated with defects such as vacancies and interstitial loops.

6.6 Conclusions

The concentration of trapped deuterium in nickel irradiated by ^3He was observed using the in-situ observation technique described in the previous chapter. The followings were concluded from the results of the experiments.

1. The trapping sites were produced in nickel by continuing the ^3He irradiation.
2. The trapped deuterium was observed at elevated temperature of 455 to 568 K, since the samples were continuously exposed to the deuterium plasma.
3. The trapped deuterium concentration increased with the ^3He dose until it became nearly saturated.
4. The density of the traps became higher at lower temperatures.
5. The trapping energy was estimated to be 0.14 eV. The trap was not associated with bubbles but would be with defects such as vacancies and interstitial loops.
6. The contribution of the trapped hydrogen to the inventory in the plasma-facing materials will be significant when the trap density is large and the concentration of the dissolved hydrogen is small.
7. The traps would also affect the permeation at non-steady state in the plasma-facing walls.

Chapter 7

Depth profiles of trapped deuterium

In the previous chapter, the trapping of deuterium in nickel bombarded by ^3He was observed, and the dependence of the trapped deuterium concentration on the bombardment dose, the trap density and trapping energy were discussed. In this chapter, the depth profiles of the traps were observed at an elevated temperature of 523 K. They were obtained by low energy bombardment of ^3He to the sample and subsequent measurements by the NRA with higher energy ^3He . Experimental results are discussed and the relation between the trap density and the amount of the radiation damages is estimated.

7.1 Depth profiles

A sample is a 0.1-mm thick nickel membrane, which is mechanically polished with a 0.3 μm alumina finish. The experimental device is the same as in Fig.5.6.

The sample was kept at 523 K and exposed to the deuterium plasma. The deuterium PDP reached the steady state and its permeation flux of $7 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$ was constant during the experiment. A probing beam of 1.7-MeV ^3He irradiated the sample at the plasma-exposure side at the 45° angle to the surface normal while the exposure of the plasma to the sample was continued. A beam current was kept constant at 200 nA ($7.0 \times 10^{16} \text{ m}^{-2}\text{s}^{-1}$). The irradiation dose of the probing beam was less than $5 \times 10^{19} \text{ m}^{-2}$ to minimize irradiation effects. It was already known in the previous chapter that few traps were produced at this dose.

The observed depth profile of deuterium is shown by the triangles in Fig.7.1.

The mean projected range of 1.7-MeV ^3He in nickel is $2.8\text{ }\mu\text{m}$ [131]. The beam irradiated the sample at 45° and the mean depth corresponding to the end of the projected range of ^3He was $2.0\text{ }\mu\text{m}$. As the ^3He ion with lower energies scarcely reacts with deuterium owing to lower cross sections, the maximum probing depth was about $1.5\text{ }\mu\text{m}$. The deuterium concentration near the upstream surface was rather high, since a large amount of deuterium was absorbed on the surface as discussed in the chapter 5.

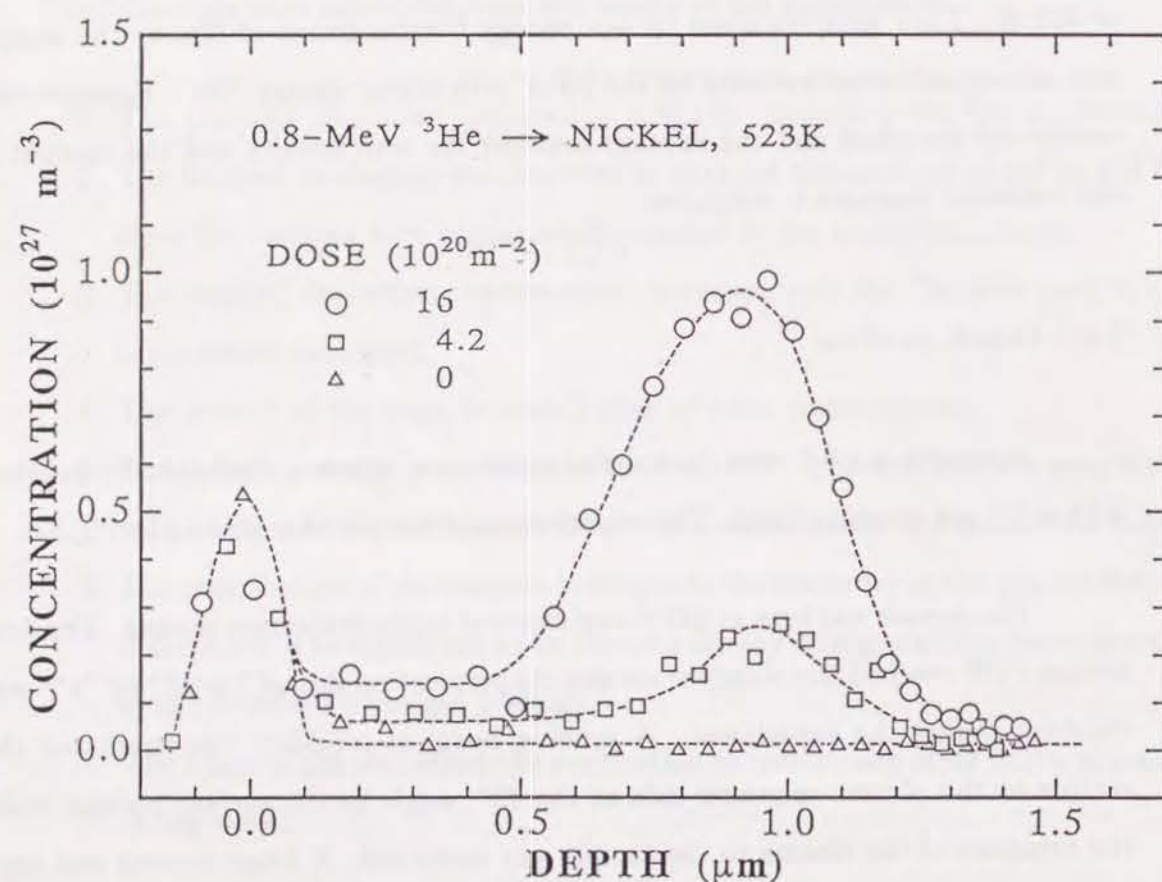


Fig. 7.1. Observed depth profiles of deuterium in nickel at 523K. The bombardment of the 0.8-MeV ^3He ion increased the deuterium concentrations as shown by squares and circles.

The permeation of deuterium was limited by the diffusion process under

our experimental conditions and the concentration of dissolved deuterium C_{su} near the upstream surface was given by Eq.(2.11) as discussed before. The value of C_{su} obtained from the steady-state permeation flux was $1.1 \times 10^{25}\text{ m}^{-3}$. The average value of the deuterium concentration between 0.2- to $1.5\text{-}\mu\text{m}$ depth was $1.2 \times 10^{25}\text{ m}^{-3}$, which agreed well with the above value. This indicated that there were few traps in the sample at first.

After the above experiment, the sample was “bombarded” with the beam of 0.8-MeV ^3He at the 45° angle to the surface normal to produce damages. We will use “bombardment” to describe the irradiation for the damage production. The beam current was 200 nA. Subsequently, the sample was irradiated by the probing beam of 1.7-MeV ^3He to obtain the depth profile. This sequence was repeated several times.

The squares and circles in Fig7.1 show the observed depth profiles with the bombardment doses of 4.2 and $16 \times 10^{20}\text{ m}^{-2}$, respectively. The observed deuterium concentration in the bulk increased with the bombardment dose and a peak appeared at a depth of $0.95\text{ }\mu\text{m}$ while no changes were seen in the concentration of deuterium absorbed on the surface.

The mean projected range of 0.8-MeV ^3He in nickel is $1.4\text{ }\mu\text{m}$ [131]. The mean depth, considering the incident angle of the beam, was then $1.0\text{ }\mu\text{m}$. It nearly corresponded to the depth of the peak. This indicated that the beam of 0.8-MeV ^3He produced traps and deuterium was trapped in them.

7.2 Trapped deuterium

Deuteriums is retained in nickel being dissolved, trapped in the bulk or absorbed at the surface. All of these deuteriums contributed to the observed depth profiles in the bombarded sample. The profile of the dissolved and absorbed deu-

terium was already known by the measurement before the bombardment, which is shown by the triangles in Fig.7.1. The profile of the trapped deuterium could be obtained by subtracting this from the observed one of the bombarded case. It is shown in Fig.7.2, which corresponds to the data shown by the circles in Fig.7.1. The trapped deuterium concentration is nearly constant below a 0.5- μm depth. Beyond that depth, however, it increases and shows a peak at the 0.95- μm depth.

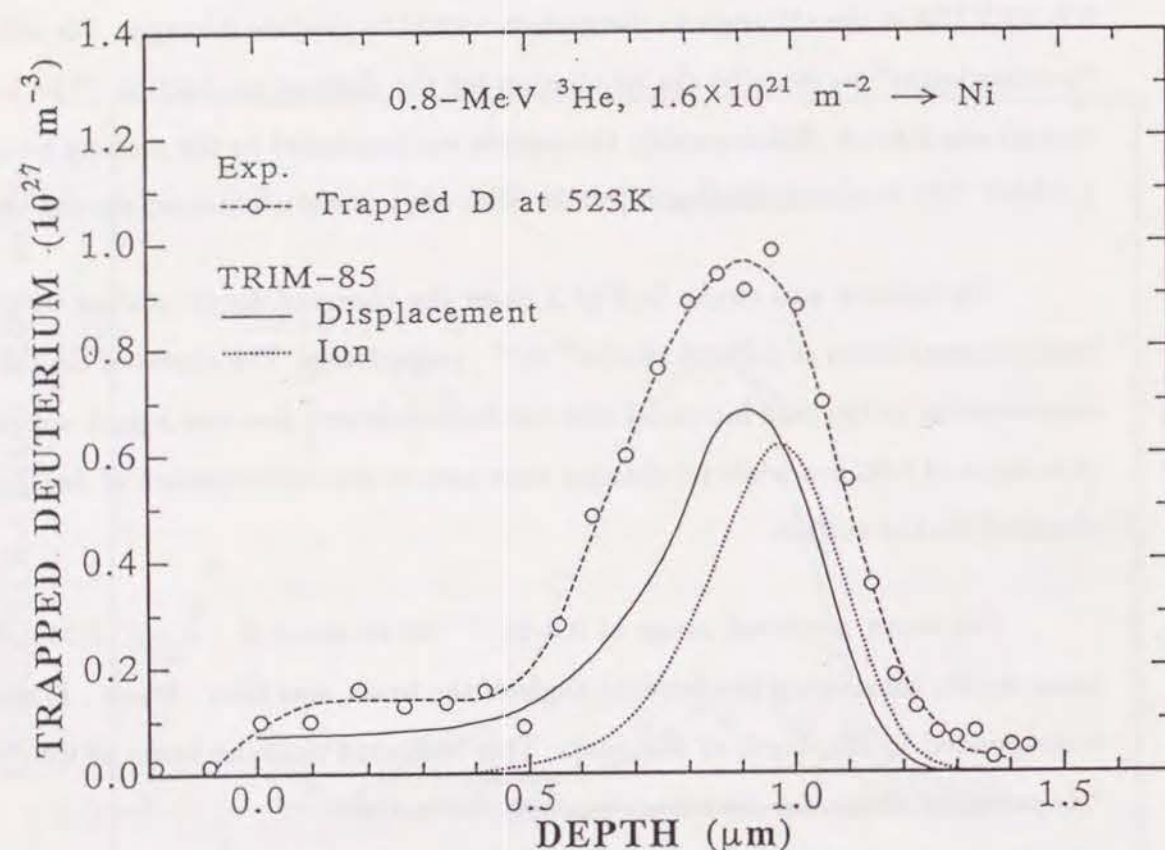


Fig. 7.2. A depth profile of the trapped deuterium (circles) after the bombardment of 0.8-MeV ^3He with $1.6 \times 10^{21} \text{ m}^{-2}$ dose. The distributions of displaced host atoms (solid line) and incident ions (dotted line) estimated by TRIM-85[153] are shown in arbitrary units.

The trapping sites for hydrogen isotopes would be associated with incident

helium ions and radiation induced defects. The former is related with the distribution of the ions and the latter is with that of atomic displacements of the host metal. In Fig.7.2, distributions of both the ions and the displaced atoms estimated by TRIM-85 code [153] are shown in arbitrary units. In the calculation, the displacement energy of the nickel atom was assumed to be 40 eV. The distribution of the displaced atoms was quite similar to the profile of the trapped deuterium. On the contrary, ^3He ions scarcely existed in the region below 0.4 μm . These indicated that the trapping sites were related with the atomic displacements.

The FWHM (full width at half maximum) of the peak of the trapped deuterium concentration shown by the circles in Fig.7.2 is 0.47 μm . The energy straggling for the probing beam and produced protons were estimated from the Bohr's theory to be 45 keV and 23 keV, respectively. These contributed to the depth resolution, which was represented by the FWHM, by 0.06 μm . The depth resolution of the detecting system other than the straggling was estimated to be 0.16 μm from the profile on the surface in Fig.7.1. Taking both factors into account, the depth resolution at 1 μm -depth is 0.17 μm and the FWHM of the peak becomes 0.43 μm . It is larger than that for the estimated distribution of the displaced atoms of 0.35 μm as shown by the solid line in Fig.7.2. This discrepancy may be attributed to migration of defects.

The profile of the trapped deuterium after the bombardment of 1.3-MeV ^3He ions up to the dose of $1.6 \times 10^{21} \text{ m}^{-2}$ is shown in Fig.7.3. The energy of the probing beam was 2.0 MeV and the maximum probing depth was 1.8 μm . The profile resembles that in Fig.7.2, but the peak shifted to deeper depth of 1.4 μm . The depths where the injected 1.3-MeV ^3He ions and the displaced atoms were mostly present were estimated by the TRIM code to be 1.53 and 1.41 μm , respectively. The latter just corresponded to the depth of the peak for the trapped concentration as shown in Fig.7.3.

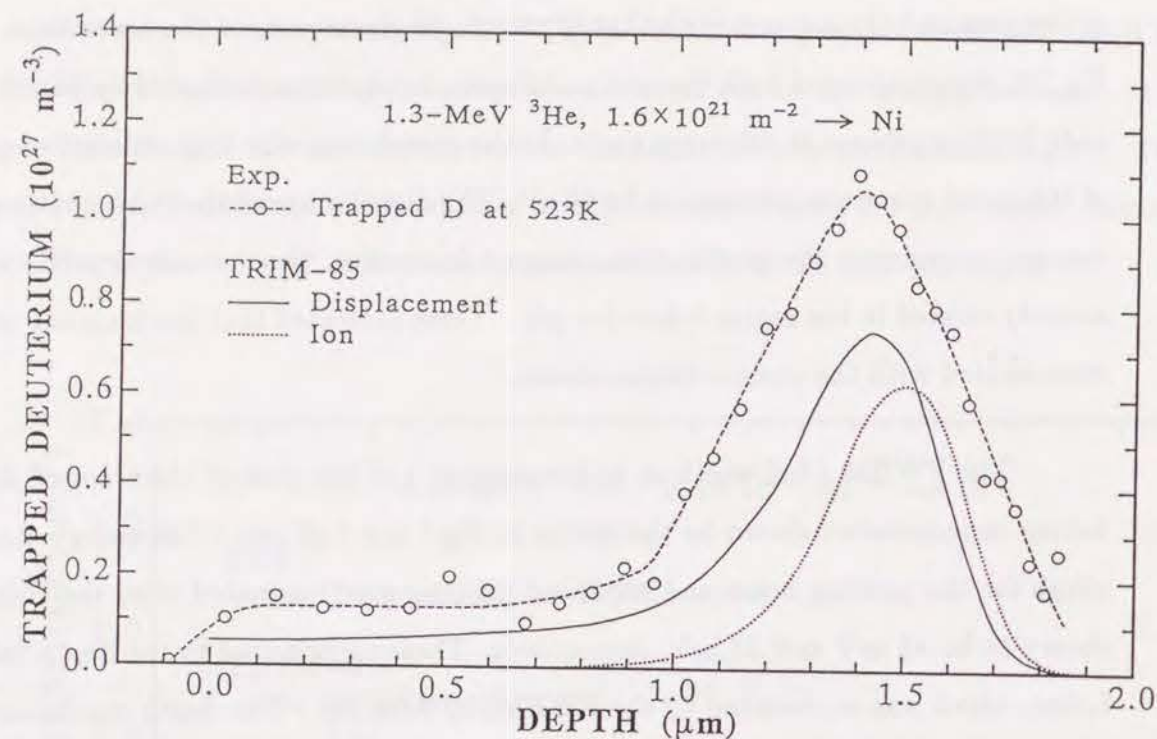


Fig. 7.3. A depth profile of the trapped deuterium after the 1.3-MeV ^3He bombardment. The estimated distributions of displaced host atoms and bombarding ^3He are shown in arbitrary units.

The areal density of the trapped deuterium was $7.2 \times 10^{20} \text{ m}^{-2}$. In the case of the 0.8-MeV ^3He bombardment of the same dose, it was $5.4 \times 10^{20} \text{ m}^{-2}$, where the bombardment dose of the ^3He ions in both cases was $1.6 \times 10^{21} \text{ m}^{-2}$. If the trapping sites were associated with ^3He ions, the number of trapped deuterium should depend on the dose, not the energy. From above results, it was concluded that the traps were defects associated with atomic displacements, and not with heliums.

7.3 Relation between traps and displacements

The relation between the trap density and the number of displaced atoms will be discussed. As the sample was continuously exposed to the deuterium plasma, the traps were mostly occupied by deuteriums under our experimental conditions as mentioned in 6.2. Hence, the trap density was assumed to be the same as the concentration of trapped deuterium.

The areal density of the trap, which is integrated the trap density from the surface to the probing depth, is plotted against the bombardment dose of ^3He in Fig.7.4. The sample temperature was 523 K and the bombardment energy was 0.8 MeV.

The areal trap density increased proportionately with the dose at first, but tended to be saturated at higher doses. A similar behavior has been seen in Fig.6.1, where the nickel sample was continuously bombarded by 1.3-MeV ^3He ions and the averaged deuterium concentration between 0.2- to 0.8- μm depth was observed at the same time. The evolution curve of the areal trap density in Fig.7.4 is analogous to that of the amorphization of silicon implanted by charged particles [154]. One of the causes of the saturation may be that no sites were left to become the trap under the high-dose bombardment. However this could not explain the fact that the shape of the depth profile was independent of the bombardment dose (see Fig.7.1). Another reason would be that the production and the disappearance rates of the traps were in balance as discussed in 6.1.

We will consider the relation in the low dose region where the areal trap density is in proportion to the bombardment dose. For the 0.8-MeV ^3He bombardment below the dose of $1.3 \times 10^{21} \text{ m}^{-2}$, the ratio of the trap density to the dose was 0.41 from Fig.7.4. The average number of the produced displacements per incident ^3He ion was estimated to be 61 by the TRIM code. The trap production rate, which

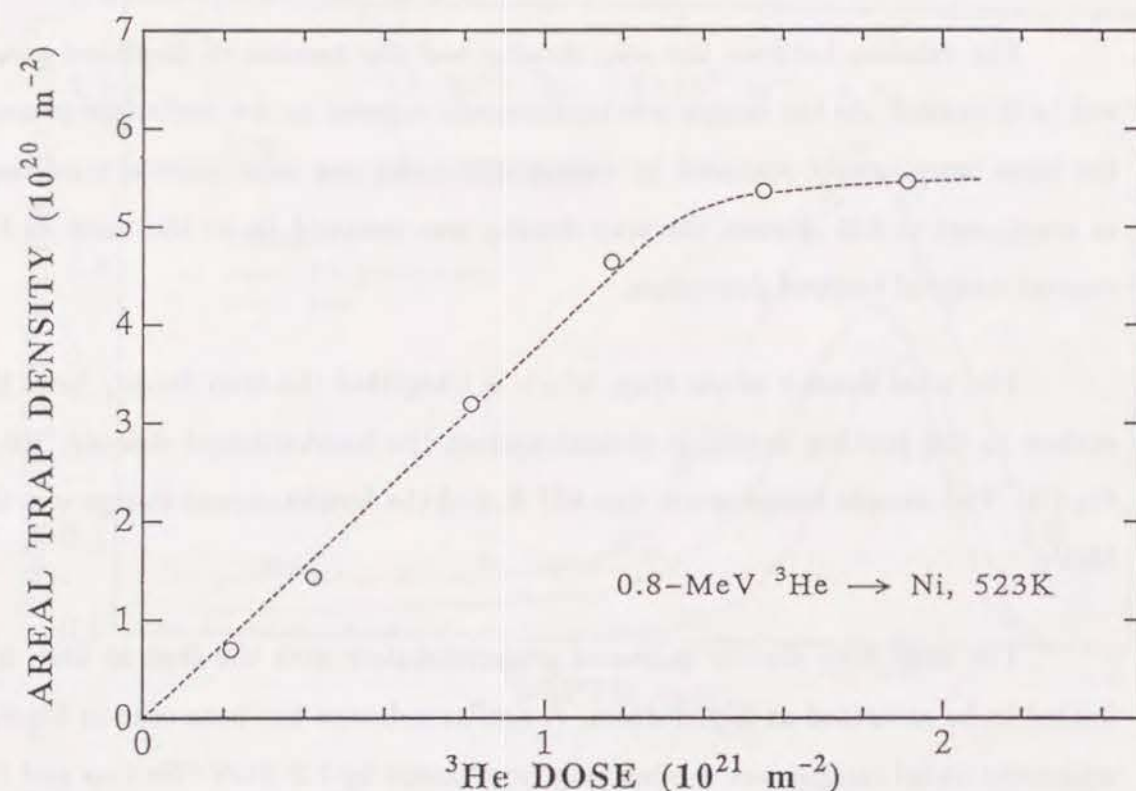


Fig. 7.4. An evolution of the areal trap density with the ^3He dose. The trap density increased linearly at low doses until it became nearly saturated.

is defined as the ratio of the number of traps to that of displaced atoms, becomes 0.0067. It is much smaller than unity, because most displaced atoms would be recombined with lattice vacancies during the short-time annealing just after the collision cascade and few defects would survive [155, 156]. The above values are listed in Table 7.1.

For the 1.3-MeV ^3He bombardment, the measurement was made only at the dose of $1.6 \times 10^{21} \text{ m}^{-2}$. This dose is slightly higher than the upper limit, up to which the trap density in Fig. 7.4 is proportional to the dose in the 0.8-MeV ^3He bombardment case. However, since the 1.3-MeV ^3He dose required for the

Table 7.1. Production rate of the traps to the displaced nickel atoms at 523 K

^3He energy (MeV)	A. Dose ($^3\text{He}/\text{m}^2$)	B. Trap density (traps/ m^2)	B/A (traps/ ^3He)	C. Displaced atoms ¹⁾ (atoms/ ^3He)	Production rate (=B/AC) (traps/atoms)
0.8	($\leq 1.3 \times 10^{21}$)	—	0.41 ²⁾	61	0.0067
1.3	1.6×10^{21}	7.2×10^{20}	0.45	65	0.0069

1) The displacement energy was assumed to be 40 eV in the TRIM-85 code.

2) The value is valid below the dose of $1.3 \times 10^{21} \text{ m}^{-2}$ where the trap density was in proportion to the dose.

saturation of the traps was about $3 \times 10^{21} \text{ m}^{-2}$ as shown in Fig. 6.1, the trap density was considered to be still proportional to the dose in this case.

As listed in Table 7.1, the value B/A, which is the ratio of the areal trap density to the bombardment dose, was slightly larger for 1.3 MeV than for 0.8 MeV. The value of C, which was the number of displaced atoms per ^3He ion, increased with the energy. As the result, the trap production rate B/AC did not depend on the incident ^3He energy. This also indicated that the traps were associated with the defects such as vacancies and interstitials and not with ^3He particles retained in the sample.

The bombardment of ^3He greatly enhanced the deuterium concentration. For example, the average value of the observed concentration up to 1.5- μm depth was $3.6 \times 10^{26} \text{ m}^{-3}$ after the 0.8-MeV ^3He bombardment with $1.6 \times 10^{21} \text{ m}^{-2}$ dose. It was thirty times as large as that of the dissolved deuterium concentration. This suggests a significant increase in the tritium inventory in the plasma-facing wall of fusion reactors, since the traps would be produced by not only heliums but also neutrons.

Neutrons penetrate deep into materials and would produce traps uniformly in the walls.

When 2.0-MeV C^+ bombarded a nickel membrane with $2.4 \times 10^{20} \text{ m}^{-2}$ dose, no trapped deuteriums were observed at 523 K. The estimated displacements was $9.1 \times 10^{22} \text{ m}^{-2}$, which was nearly the same as that in the 0.8-MeV $^3\text{He}^+$ case. The production of the traps is not simply related with the atomic displacement but also with the bombarding ion. According to Wilson et al. [157, 158], a few helium particles and a vacancy in fcc metals form a stable complex. It may be responsible for the presence of the traps in the ^3He bombardment case.

There have been few works on the hydrogen trapping at elevated temperatures and little has been known about the traps. The in-situ observation technique is a new method that can provide basic data for developing theories on the mechanisms of the hydrogen trapping and its production.

7.4 Conclusion

By applying the in-situ observation technique, the present work first observed the depth profiles of the trapped deuterium under the condition where there was an equilibrium between the dissolved and the trapped deuterium at an elevated temperature of 523 K. The depth profiles of the trapped deuterium in nickel bombarded by ^3He ions agreed well with the distributions of the displaced host atoms. It was found the traps were associated with the radiation damage of the atomic displacements.

At low bombardment doses, the production rate of the traps to the atomic displacements was constant and independent of the incident energy. It was shown that the in-situ observation of deuterium, where the exposure of the deuterium plasma and the NRA were conducted at the same time, could be used for the quantita-

tive studies not only on the thermal behaviors of deuterium such as diffusion and recombination but also on the deuterium trapping in metals.

Chapter 8 Summary

With respect to the tritium technology in the plasma-facing walls of fusion reactors, basic experiments on the PDP (plasma driven permeation) of hydrogen isotopes were conducted using the small rf-plasma device and Heliotron E. The permeation flux of the PDP in both the devices were very large and they were strongly influenced by the surface impurities such as oxygen.

In the present work, the in-situ observation technique was developed, where the PDP flux and the depth profiling of deuterium by the NRA (nuclear reaction analysis) were observed at the same time. The technique gave the deuterium concentration near the plasma-exposure surface, which could not be observed by the ordinary permeation method. Thermal behaviors of deuterium such as diffusion and recombination in nickel were studied knowing the dissolved deuterium concentrations. The depth profiles of trapped deuterium in nickel, which was bombarded by ^3He ions, were also observed using this technique. Due to the continuous exposure of the deuterium plasma to the sample, there was an equilibrium between the trapped and the dissolved deuterium.

The results and conclusions in each chapter were summarized below:

Chapter 1 Studies on thermal behaviors of hydrogen in metals such as the ordinal permeation (GDP), the PDP and the trapping were reviewed. The objectives of the present work were described with respect to the thermal behaviors of hydrogen in the plasma-facing walls of fusion reactors.

Chapter 2 A general equation to describe a time-dependent change in the trapped hydrogen concentrations was derived assuming that the traps were associated

with lattice defects. This equation includes all models which have been proposed till now. The equations for hydrogen diffusion, recombination and permeation were also explained.

Chapter 3 The deuterium PDP was observed using a small rf-plasma device with a glass discharge tube. The permeation flux of the PDP was found to be much larger than that of the GDP under the same pressure of deuterium gas. Some important characteristics of the PDP from the plasma were shown; the permeation was affected by impurities, neutral atoms mainly contributed to the PDP and the isotope effect was not different from that in the GDP. Another experiment was performed to estimate pulse operations of the large plasma devices. Transient behaviors of the permeation could be well reproduced by numerical calculations.

Chapter 4 An experimental device was installed to Heliotron E, one of the largest helical plasma devices, to study the deuterium PDP from the steady-state plasma for the discharge cleaning. The noticeable PDP through nickel was observed, and its permeation flux was affected by the particle recycling of deuterium and impurities. The progress of the discharge cleaning would be estimated from the permeation flux.

Chapter 5 The in-situ observations of deuterium were conducted, in which the permeation flux of the PDP and the deuterium depth profile by the NRA were observed at the same time. It was shown that the large permeation flux in the PDP was caused by the high concentration of the dissolved deuterium. In the experiments with nickel membranes, the PDP was the diffusion-limited permeation, and both the recombination coefficient and the diffusion coefficient in nickel were determined. The in-situ observation could be used for determining the diffusion coefficient of deuterium in metals without any effects of the surface impurities.

Chap 6 The concentrations of trapped deuterium in nickel, which was continuously bombarded by ^3He ions, were observed at elevated temperatures of 455 to 568

K, using the in-situ observation technique. Both the trap density and the trapping energy were determined by the equations derived in the chapter 2. Effects of the traps on the PDP and the inventory of the plasma-facing walls were also discussed. The traps were not the bubbles but associated with the radiation damages.

Chapter 7 The in-situ observation was performed with nickel membranes, which were prebombarded with ^3He ions. As the trapped deuterium and the dissolved one were in equilibrium, the depth profiles of trapped deuterium were observed at an elevated temperature of 523 K. Comparing the depth profiles with the estimated distributions of the displaced host atoms, the traps were found to be associated with the atomic displacements. The production rate of the traps to the displacements was determined. The in-situ observation is a new method that can provide useful information on the hydrogen trapping.

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