

STUDIES ON TRITIUM RETENTION IN PLASMA FACING MATERIALS

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Tritium retention behavior on an isotropic graphite was studied by exposure with high flux atomized D/T particles. From analysis of thermal desorption spectra of retained tritium it was shown that tritium implanted into graphite existed in two different states. One was trapping to defects and the other was C-T bond. The amount of tritium retained in graphite was in proportion to a half power of total incident fluence and no saturation was observed up to 10^{26} atoms·m⁻². The total tritium retention in the sample exposed to atomized D/T particles with total incident fluences of 10^{25} - 10^{26} atoms·m⁻² were estimated 1×10^{22} - 4×10^{22} atoms·m⁻².

Moreover, the existing states of deuterium implanted into Be and W have been investigated using the X-ray Photoelectron Spectroscopy (XPS). The XPS experiments showed some plasmon energy shifts for Be and W, which implied that deuterium implanted exist in the lattice of those metals.

1. INTRODUCTION

From the viewpoint of tritium safety and accountability in fusion reactors, estimation of tritium inventory in plasma facing materials such as graphites, Be, W, etc. is one of important subjects of fusion tritium technology. To estimate the tritium inventory, physicochemical behavior (existing states, migration, release, etc.) of tritium implanted in the plasma facing materials should be investigated.

Graphite is one of the candidates for the plasma facing materials of ITER, and also the most widely used first wall material in current tokamak devices because of its high performance of plasma confinement and good thermal properties. In the past several years, many studies on the retention of hydrogen isotopes in graphites¹⁻⁸ have been made. However, there are fairly large discrepancies among the data reported. They can be attributed to use of protium or deuterium in most the work and differences in sort of graphite sample, and plasma exposure conditions (flux, fluence, energy, temperature, impurities in plasma, etc.). Hucks et al.⁹ examined the retention of sub-eV atomic hydrogen using a tracer amount of tritium and reported a much larger retention than that in the studies with protium and deuterium. Youle et al.¹⁰ measured the retention of protium and tritium atoms of thermal energies incident on pyrolytic graphite by thermal desorption spectrometry to determine its fluence and temperature dependence in the range 4×10^{19} - 2×10^{24} atoms·m⁻² and 480-820 K.

However, there is still little effective data available on estimation of tritium amount retained in plasma facing materials an ITER (International Thermonuclear Experimental Reactor) equivalent environment with a high flux ($\geq 10^{23}$ atoms·m⁻²s⁻¹) atomized D/T particle irradiation.

The present studies have been initiated to obtain effective data for estimation of tritium retention in graphites. An apparatus has been developed for exposure experiments of atomized D/T particles with a high flux.

In the present paper, retention behavior of tritium implanted in graphite by exposure of RF tritium plasma has been studied. Based on the experimental results, the tritium existing states in the graphite and the release kinetics are discussed.

II. EXPERIMENTAL

A. Tritium plasma exposure experiment

Figure 1 shows a schematic drawing of the apparatus used for deuterium plasma exposure experiments. The apparatus consists of three sections for plasma exposure, thermal desorption and gas analysis respectively. The sample used was high density isotropic graphite plate (ETP-10, Ividen Co., 10×10×0.4 mm). The sample was degassed at 1473 K for 2 hours under vacuum below 10^{-4} Pa before plasma irradiation.

Plasma was generated by RF discharge (13.56 MHz, 50 W, power supply and control with JEOL model JEH-005TS). During plasma exposures deuterium pressure in

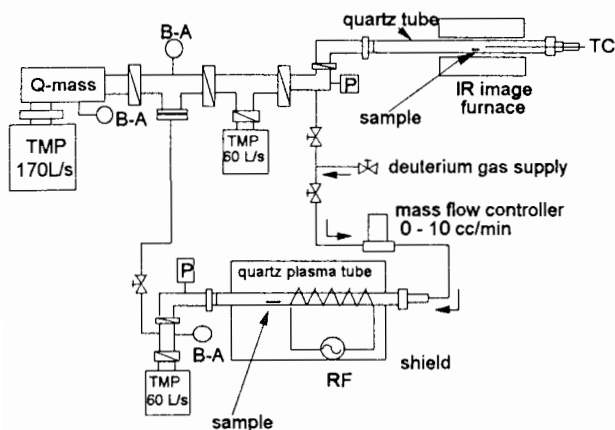


Fig. 1. The schematic drawing of the apparatus for deuterium plasma exposure

the quartz plasma tube and deuterium flow rate were kept at about 4 Pa and about $10 \text{ cm}^3/\text{min}$, respectively.

After plasma exposure at room temperature, the sample was heated isochronically from 300 K to 1473 K at temperature ramp of 5–100 K/min. The gas released from the sample was analyzed by a quadrupole mass spectrometer (MSQ-400 ULVAC Co.).

Based on the experiences obtained with the systems used for deuterium plasma exposure experiments, a new apparatus for D-T plasma exposure experiments has been developed as shown in Fig. 2. Plasma exposure and sample heating can be performed simultaneously. Plasma was generated in a quartz tube (10 mm inner diameter, about 200 mm length), which was installed inside the stainless steel main chamber, by RF emission (13.56 MHz, 50 W) from a coil shaped antenna which surrounded outside of the plasma tube about 100 mm above its end.

A graphite sample disk (10 mm in diameter and about 0.6 mm in thickness) was placed on a quartz sample holder plate and capped with the plasma tube. The sample was heated from the opposite side of plasma emission by a furnace consisting of a halogen lamp, ellipsoid reflection mirror and a quartz rod light guide. The samples were preheated and degassed at 1270 K in vacuo ($\sim 10^{-3}$ Pa) for two hours. The $\text{D}_2\text{-DT}$ (D:T=1000:1) mixture gas was supplied continuously from the top of the plasma tube at a flow rate of $0.3 - 1.5 \text{ cm}^3/\text{min}^{-1}$. The pressure in the plasma tube was kept at 6.7 Pa by balancing the inlet flow and the gas leakage at the contact part of the plasma tube and the quartz sample holder plate. The main chamber was evacuated with turbo-molecular pump at about 10^{-3} Pa.

Taking account of the condition above and that the graphite sample was enclosed totally in quartz wall with very low hydrogen atom recombination factor ($\sim 10^{-4}$),

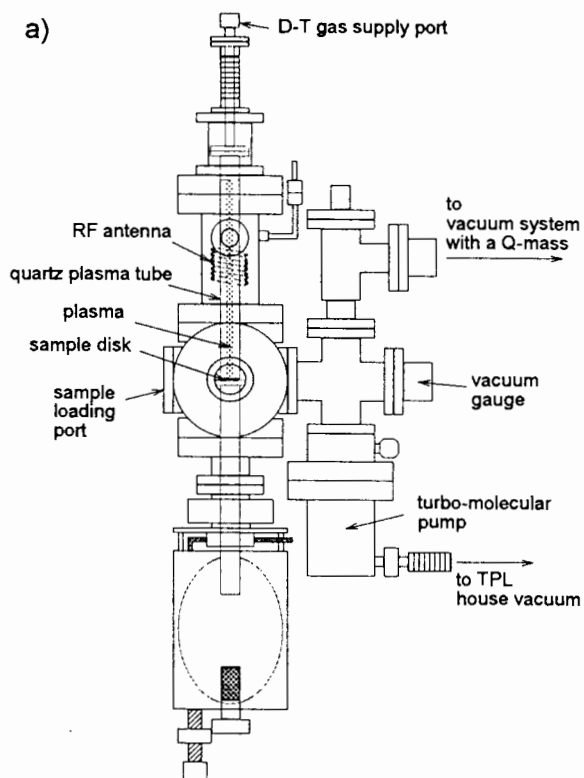


Fig. 2. The apparatus for D-T plasma exposure experiments

the dominant species incident upon the sample can be atomized D/T particle with low energy (≤ 100 eV). We assumed the flux of the atoms incident upon the graphite sample which occupied the cross section of the plasma tube at the end was equivalent to the D-T gas flow rate, i.e. flow rate of $0.3-1.5 \text{ cm}^3/\text{min}^{-1}$ corresponded to atom flux of $4.6-11.4 \times 10^{21} \text{ atoms} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at the sample surface. D-T plasma exposures were performed for 1 hour and 4 hours, and total fluences were $1.6 \times 10^{25} \text{ atoms} \cdot \text{m}^{-2}$ and $1.6 \times 10^{26} \text{ atoms} \cdot \text{m}^{-2}$ respectively.

After exposure, dry air purge and evacuation of the main chamber were repeated for a few times to remove tritium absorbed on the wall inside the chamber. After the tritium level in the purged dry air reached to the background, the sample was heated at about 970 K in the dry air flow for combustion. Tritiated water in the dry air flow was trapped with two water bubblers and a cold trap. No tritium level increase of the ion chamber at downstream of those traps was observed during combustion. Total tritium amount in the sample was obtained by measurement of the trapped tritiated water with a liquid scintillation counter system.

B. XPS experiments

For the experiments 3 different samples have been used, pure sintered tungsten and beryllium containing

0.9% of oxygen. The experiments have been performed in a commercial XPS-apparatus PHI 5600. The apparatus has been equipped with a dual gas ion gun, suitable for use either with argon or with deuterium.

First the samples have been cleaned by Ar-sputtering, that no surface contamination was anymore detectable. Using Mg K α radiation the XPS-spectra including the loss structure of the photoelectron peaks and the X-ray excited Auger spectra have been recorded. Afterwards the treatment with a deuterium ion beam of 3 keV energy has been performed with increasing ion dose, followed by a subsequent in-situ measuring of the treated surface.

III. RESULTS AND DISCUSSION

A. Tritium plasma exposure experiment

In the thermal desorption spectra (TDS) of D₂ from the samples exposed to deuterium plasma in the closed system, two peaks were observed at different temperatures, one at about 800 K and the other at about 1250 K (Fig. 3). These two peaks can be attributed to two different states of the deuterium trapped in the graphite. Following Readhead's theory¹¹ for analysis of isochronal thermal desorption, the activation energies of the two different states were determined to be 1.8 eV

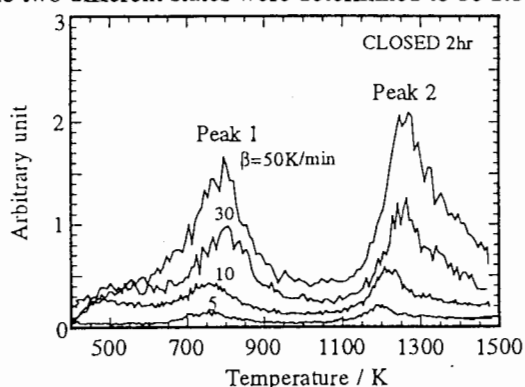


Fig. 3 TDS of D₂ in the closed system (plasma exposure time : 2 h)

(800 K) and 3.9 eV (1250 K), respectively.

Activation energy of hydrogen adsorption on graphite reported were varied from 0.2–2.2 eV.^{12–15} The activation energy for the peak at 800 K in our study was in this range. Concerning the peak at 1250 K, the binding energy of C–H bond is about 4 eV. Accordingly it can be said that the state with the release rate maximum at about 800 K corresponds to release of D from a trap site such as lattice defects in graphite and the other state with release rate maximum at about 1250 K does to that from a chemical bond between carbon and deuterium. In our results, it was also shown that both of the desorption

process of D₂ was a first-order reaction which implied that detrapping of deuterium atom from graphite was rate-determining process, while Ashida et al.³ and Tanabe et al.⁸ reported those were second-order reaction.

In the experiments with the flow system, the TDS of D₂ had also two peaks of release rate maximum at same temperature (Fig. 4) as with the closed system. However, the ratio of the peak intensity at around 800 K to the one at around 1250 K with the flow system was larger than that with the closed system.

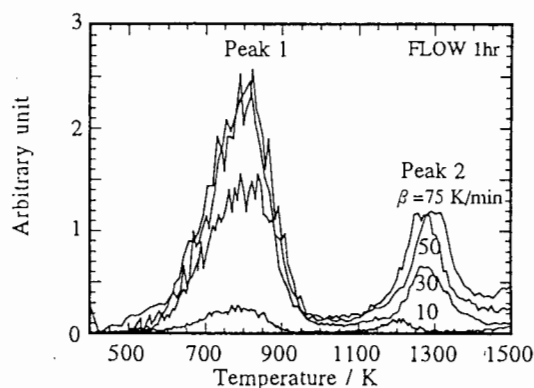


Fig. 4 TDS of D₂ in the flow system (plasma exposure time : 1 h)

Mass analysis of the exposure gass showed that in flow system D₂ was dominant species and it did not change during plasma exposure, while in the closed system D₂ decreased and other species like hydrocarbons, C, and CO progressively increased. The difference of gas composition change was also observed as change in the plasma color of the both systems. Consequently, in the closed system, graphite was exposed other species besides deuterium in the most of time for exposure. The difference in the peak ratio of the TDS between both systems is probably concerned with gas composition in plasma exhaust gas. In the closed system once hydrocarbons were generated in plasma, they could not be removed from the chamber and their concentration increased. On the other hand, in the flow system hydrocarbons generated in plasma were removed by continuous evacuation, so their concentration remained constant and at very low level. Therefore, the amounts of the hydrocarbons deposited to the graphite sample, which were the source of deuterium bonded to carbon, are different between the systems. Accordingly this shows that plasma generated in the flow system is more practical to simulate the first wall circumstances.

In fig. 5, the relationship between plasma exposure time and the integration of the signal intensity of TDS of D₂, which is supposed to be in proportion to the total amount of D₂ retained in the graphite samples, is

shown. As shown in fig. 5, the total amount of D_2 retained was in proportion to almost a half power of plasma exposure time. As the deuterium gas flow rate was constant, this result consistent to the results of Tanabe⁸ and Hucks⁹ implies that release of D_2 related to diffusion process. From rough estimation by assuming one sixth of deuterium amount flowing in the quartz plasma tube can be incident upon the sample, that of 5 hours plasma exposure corresponds to total incident atom fluence of 2.7×10^{26} atoms·m⁻². This shows that up to this fluence no saturation was observed during the exposure at room temperature.

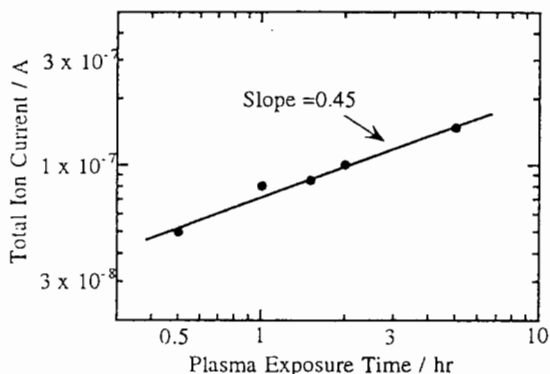


Fig. 5. The relationship between deuterium plasma exposure time and total amount of D_2 released (with the flow system, temperature ramp : 30 K/min)

In fig. 6 the total (D+T) retention obtained by D-T plasma exposure experiments is shown with the results of the other works. The total tritium inventory in the graphite samples obtained for total incident atomic fluences of 10^{25} – 10^{26} atoms·m⁻² were 1×10^{22} – 4×10^{22} atoms·m⁻² respectively. The data obtained here are almost on the line extrapolated from the results of Hucks et al⁹, which were in proportion to a half power of total incident fluence as similar to our results with deuterium. This implies that at room temperature tritium retention in graphite is not saturated yet and concerned to a sort of diffusion process. Tanabe et al. suggested this diffusion process concerns growth of the saturated layer. However, assuming such saturated layer growth, the diffusion coefficient roughly estimated from our results was about 1×10^{-17} m²s⁻¹, which is much larger than the value of 7×10^{-24} m²s⁻¹ deduced from the equation they gave. So we suppose at room temperature probably diffusion of tritium through another path besides bulk, for example grain boundary or small pore, are dominant.

B. XPS experiments

The X-ray Auger Electron Spectroscopy (XAES) spectra of W and Be show no changes due to the

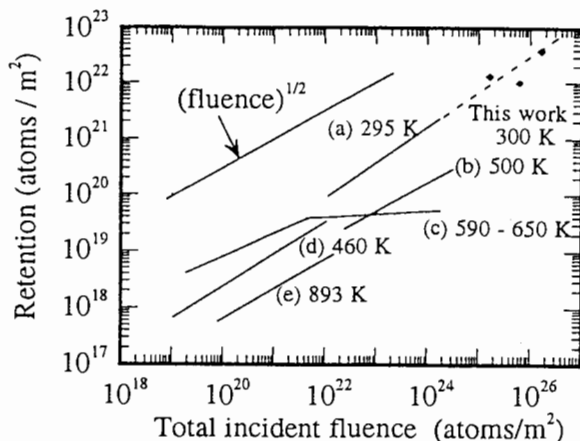


Fig. 6. Retention in graphite as a function of total incident fluence.

- (a) protium and tritium (2.5×10^{-3} %) on pyrolytic graphite⁹
- (b) protium and tritium (2.5 – 30 %) on pyrolytic graphite¹⁰
- (c) protium and tritium (5 – 60 %) on pyrolytic graphite¹⁰
- (d) & (e) deuterium on ETP-10⁸

deuterium ion bombardment indicating, that no chemical reaction between D and W or Be occurs. Additionally there is no change in the photoelectron peak either, verifying the XAES results.

The energy loss structure of the photo electron peaks show significant differences between the investigated materials due to D^+ -radiation, as shown in Fig. 7. For tungsten the plasmon energy is increasing from 22.3 eV to 23.3 eV due to the ion beam treatment. No such behavior has been recorded for beryllium.

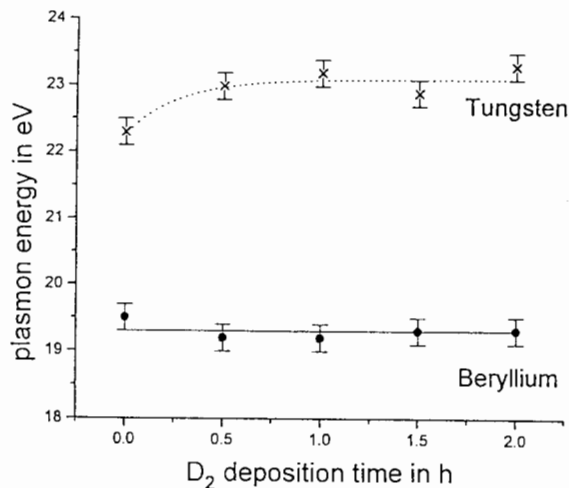


Fig. 7 D_2 -bombardment time dependence of Plasma energy of Be and W

These results can be explained by different mechanisms of incorporation of deuterium atoms in the matrix materials. For W and Be the D-atom are soluted

in the metal lattice without forming a chemical compound. The increase of the electron density due to the incorporated D causes the increasing plasmon energy in tungsten. In Be the effect is, probably due to lesser amount of incorporated deuterium, not strong enough to be detected with the used method.

IV. CONCLUSIONS

The retention of deuterium or a mixture of deuterium and tritium atoms of low energies and high flux incident on isotropic graphite at room temperature has been studied.

Moreover, the existing sites of deuterium implanted into Be and W have been investigated using the X-ray Photoelectron Spectroscopy (XPS).

From the results obtained here, the followings can be concluded.

- (1) Deuterium retained in graphite exists in two states, which are related to the two peaks in the thermal desorption spectra of D_2 , at temperatures of about 800 K and about 1250 K.
- (2) Activation energies of deuterium desorption process obtained for the two states above were 1.8 eV for that of the peak at 800 K and 3.9 eV for that of the peak at 1250 K. The former can be attributed to the activation energy of detrapping from trap site deuterium and the latter to that of dissociation from the chemical bond with carbon.
- (3) As a method to measure total amount of hydrogen retention in graphite, the closed system, in which deuterium gas was enclosed during plasma exposure, seems convenient because it can be known by pressure drop in the plasma chamber. But the closed system is not suitable to simulate the real first wall circumstances because the hydrogen plasma can be poisoned by impurities generated by plasma-surface interaction.
- (4) The results obtained with the flow system shows that deuterium atoms are retained in proportion to a half power of total incident fluence and no saturation was observed up to 10^{26} atoms·m⁻².
- (5) The total retention in the graphite samples exposed to atomized D/T particles with total incident fluences of 1.6×10^{25} and 1.6×10^{26} atoms·m⁻² were 6.5×10^{21} and 1.8×10^{26} atoms·m⁻², respectively.
- (6) The results of XPS show a clear difference in the incorporation mechanism of deuterium atoms in W and Be. For W and Be the deuterium is soluted in the lattice without creating chemical bondings with the matrix materials. Only the mechanism and as well as the amount of incorporated D is due to the unlike lattice structures different.

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