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Deuterium trapping in carbon fiber composites exposed to D plasma

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ABSTRACT

Deuterium trapping in carbon fiber composite N11 and pyrolitic graphite PG99 irradiated with plasma ions and electrons was examined with thermal desorption spectrometry. It has been found that the deuterium trapping takes place even at ion and electron energies of about 10 eV. For equal ion fluences, the deuterium retention and probability of CD_4 formation are higher for ion irradiation at lower ion flux. Peculiarities of the deuterium retention and CD_4 formation are explained; driving forces and mechanisms of the D trapping are discussed.

1. Introduction

Hydrogen isotope retention is a critical issue for future fusion devices having plasma facing components made from carbon fiber composites (CFC). It becomes especially important for ITER because tritium inventory in the vacuum vessel should be limited. Hydrogen isotope trapping and retention in graphites and CFC have been studied in a number of experiments performed in tokamaks [1] and laboratory ion beam and plasma devices [2,3]. However, flux, energy and temperature dependences of the hydrogen trapping and influence of plasma impurities on the hydrogen retention have not been measured and analyzed properly. Mechanism of hydrogen trapping has not been satisfactory explained.

The paper presents data on deuterium trapping in CFC and pyrolitic graphite (PG) irradiated with plasma ions and electrons.

2. Experimental

The experiments were performed in a thermal desorption stand intended for irradiation of samples with plasma ions and electrons and for measurement of the amount of retained gases by the method of thermal desorption spectrometry (TDS) [3]. Deuterium discharge was ignited in an electrode system composed of heated cathode, preliminary anode and anode. The preliminary measurements showed that plasma consisted mainly of the D_2^+ ions (82–85%), and the remaining part represented by D_1^+ and D_3^+. Thus, experimental results were analyzed assuming sample irradiation solely with D_2^+ ions.

The samples with dimensions of $10 \times 10\ \mathrm{mm}^2$ and 1 mm thickness were made of three dimensional CFC N11 and pyrolitic graphite PG99. The samples of both materials after machining were cleaned in alcohol in ultrasonic bath and annealed in vacuum. Irradiated surface of PG samples was oriented in parallel to hexagonal planes. To provide irradiation with plasma ions, a negative bias varying from potential of -10 V to -1000 V relative to plasma was applied to the samples. Ion irradiation was performed up to a fluence of $5 \times 10^{23}\ \mathrm{D/m^2}$ at ion fluxes of 2×10^{19} and $1 \times 10^{20}\ \mathrm{D/m^2\,s}$. On the other hand, to irradiate the samples with electrons, a positive potential of 12 V was biased. In doing so, electron fluence and flux were $1 \times 10^{25}\ \mathrm{e/m^2}$ and $1 \times 10^{20}\ \mathrm{e/m^2\,s}$, respectively. During ion or electron irradiation, the sample temperature was 450 ± 10 K. For both preliminary annealing and TDS analysis, the samples were heated up to 1650 K by thermal irradiation from a heated tungsten wire installed behind the sample underside. The sample temperature was controlled by a W–W–Re thermocouple placed in a hole made on the lateral face of the sample.

During the TDS, the sample was heated at a ramping rate of 5 K/s and release rates of D_2 and CD_4 molecules were monitored with the help of a monopole mass-spectrometer of MCX-4 type. For absolute calibration of mass-spectrometer the gas output from the implanted sample was modeled by gas flow through the calibrated leakage. It allowed an establishing of interrelations between the gas flow (D_2, CH_4) through leakage, the pressure in the experimental chamber and the signal of the MMS. For determination of sensitivity of CD_4 registration the calibration data for CH_4 were used with allowance made for their mass difference.

3. Results and discussion

3.1. Deuterium trapping under high-energy ion irradiation

The energy dependence of the amount of deuterium released as D_2 and CD_4 molecules from the CFC and PG irradiated with D ions

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at various energies (Fig. 1) demonstrates clearly that the deuterium retention decreases in both materials when the ion energy reduces from 1000 to 200 eV/D. In should be noted that the difference in the deuterium retention for the CFC and PG samples is not substantial.

Main peaks in D_2 thermal desorption spectra (Fig. 2) for the samples irradiated with deuterium ions at relatively high energies (from 500 to 1000 eV/D) are located in the temperature ranges 900–1000 K and 1050–1150 K with shoulders between 1200 and 1300 K. Begrambekov et al. [4] have analyzed a number of papers dealing with measurements of TDS spectra and concluded that temperatures of TDS peaks depend on the irradiation conditions and reflect to some extent the structure of the near-surface layer of irradiated material. In particular, they associate TDS peaks at 900–1000 K with traps created by keV ions in the stopping zone, i.e. at depths damaged and modified by the implanting ions. They have additionally shown that the high temperature peaks and/or shoulders relate to detrapping of hydrogen from traps in non-damaged layers behind the stopping zone. As can be seen in Fig. 2, both parts of D_2 TDS spectra increase with the ion energy. Thus, one can say that the deuterium trapping in the high-energy irradiated samples (HEIS) occurs both in and behind the stopping zone and depends on the kinetic energy of deuterium ions. This type of trapping can be named as 'kinetic trapping'.

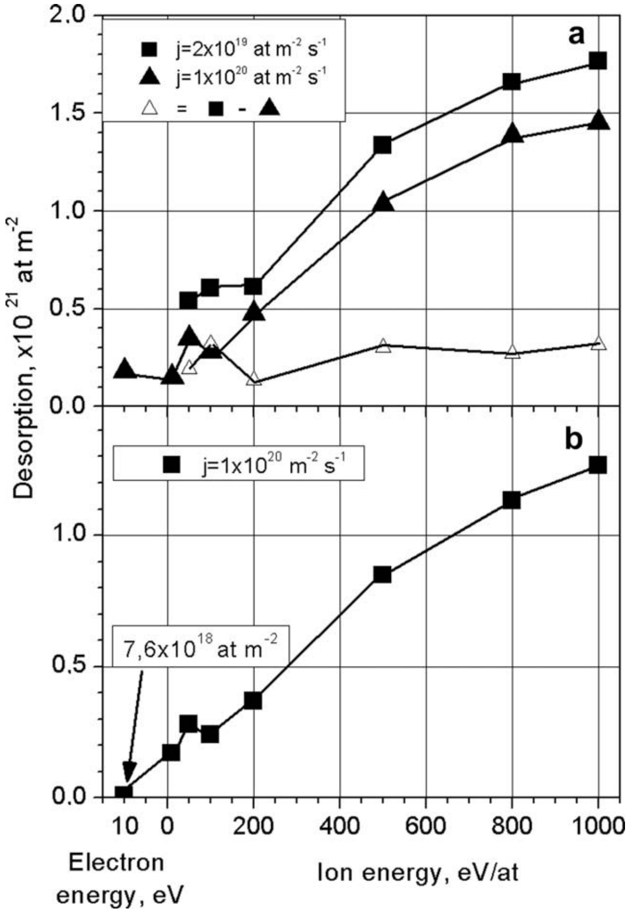

Fig. 1. Amount of deuterium desorbed as D_2 and CD_4 molecules from CFC N11 (a) and PG (b) as a function of an energy of impinging ions or electrons. The difference in the deuterium retention for the CFC N11 irradiated with ions at ion fluxes of 2×10^{19} and 1×10^{20} D/m^2 s is also plotted (a).

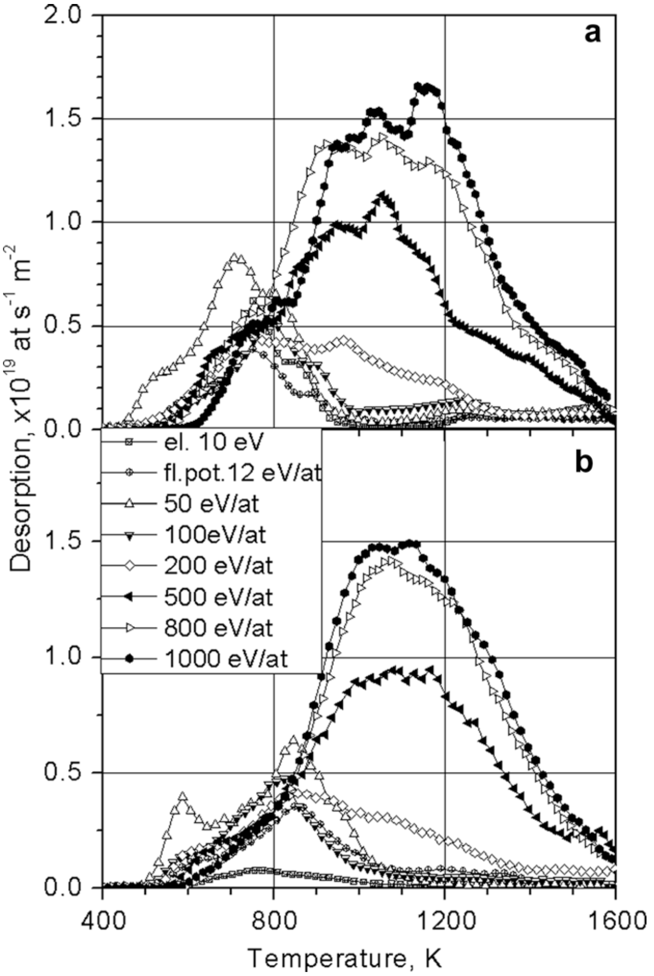

Fig. 2. Thermal desorption spectra of deuterium release as D_2 molecules from CFC N11 (a) and PG (b) irradiated with ions at various energies and electrons (the ion flux is 1×10^{20} D/m^2 s).

3.2. Deuterium trapping under low-energy and electron irradiation

At ion energies below 200 eV/D, the decrease of the deuterium retention becomes inessential (Fig. 1). A noticeable desorption from the CFC and PG samples is observed both after plasma exposure under potential of about −10 V and irradiation with electrons at an energy of 12 eV.

Main TDS peaks for the low-energy irradiated samples (LEIS) are situated in the temperature range 700–850 K (Fig. 2). The difference in the TDS peak positions for the LEIS and HEIS indicates that traps which are responsible for deuterium accumulation in the LEIS differ from those in the HEIS. Low-energy ions and electrons cannot create radiation induced traps through knock out collision with carbon atoms. Therefore, it may be concluded that deuterium is captured at active centers created due to inelastic interaction of ions and electrons with surface. One can propose that these active centers initiate dissociation of deuterium molecules sorbing on the surface, penetration of D atoms through the surface and their capture. The trapping at the active centers can be called as 'potential trapping'. The low-energy ions penetrating the surface are trapped in the same traps. Efficiency of low-energy trap formation and filling seems to be at its maximum, when impinging ions stop in the near-surface region, and decreases, as the ion penetration depth increases. It should be noted that inelastic low-energy interactions provides hydrogen trapping in some other cases. For example, hydrogen is trapped on the graphite surface at the expense of energy of water molecule interaction with graphite in the course of air exposure [5].

Peaks and shoulders observed at temperatures in the range 500–600 K exist in the TDS spectra obtained both for the LEIS and HEIS (Fig. 2). Based on our results, it is difficult to reveal the nature of these TDS peaks. However, a peak in the same temperature range was found in TDS spectra for CFC exposed to the air [5]. Thus, one can assume that relevant traps are also formed by the mechanism of 'potential trapping'.

Some part of deuterium diffuses into the bulk of the CFC and can be trapped at depths far behind the ions range. This mechanism is not valid for the dense PG structure. As a result, a peak in the temperature range 1200–1400 exists in TDS spectra for the CFC and absent in similar spectra for the PG.

3.3. Time dependence of deuterium trapping

Irradiation of the CFC samples with deuterium ions at low ion flux of 2×10^{19} D/m^2 s to a fluence of 5×10^{23} D/m^2 leads to higher deuterium retention as compared to the irradiation at high ion flux of 1×10^{20} D/m^2 s to the same fluence. This fact is observed for ion energies in the range from 10 to 1000 eV/D (Fig. 1). For fixed ion fluence, trapping of impinging ions does not depend on duration of the ion irradiation, whereas the probability of D_2 dissociation and penetration of D atoms into the near-surface layer increases with time of deuterium–graphite interaction. One can believe that the time (or ion flux) dependence of the deuterium trapping both in the LEIS and HEIS is explained by the mechanism of 'potential trapping'.

Increase of irradiation time results in growth of all parts of TDS spectra of HEIS, indicating that D atoms penetrating graphite by potential mechanism are trapped in the traps created by fast ions in the stopping zone. It is obviously, that number of deuterium traps created in the ion stopping zone of HEIS increases with increase of ion energy. But the amount of deuterium additionally trapped in longer experiments is practically the same for ions with different energies (Fig. 1). Thus, one can believe, that dissociation of deuterium molecules and penetration of deuterium atoms into graphite is the limiting stage for filling the traps in the stopping zone.

3.4. CD_4 formation and desorption

The fraction of deuterium released as CD_4 molecules from the CFC and PG samples irradiated with D ions is about 0.05 at the ion energy of 50 eV/D and increases up to about 0.16 at the energy of 1000 eV/D. Noticeable CD_4 desorption was detected from the CFC samples irradiated with low-energy ions or irradiated with electrons (Fig. 3), whereas the CD_4 desorption rate from the PG samples irradiated at the identical conditions was below the detection limit (5×10^{11} molecules/m^2 s). These findings show that CD_4 molecules are formed solely in carbon structures with high level of defects initially exist in the matrix (CFC) or/and created during energetic ion irradiation (CFC and PG).

As illustrated in Fig. 4, CD_4 peak in the TDS spectra follows position of the main peak of D_2 spectra and shifts to higher temperature as the ion energy increases (compare Figs. 2 and 4). One can see that CD_4 desorption occurs after desorption of remarkable amount of deuterium already. Porous and microchanels created at that time seem to promote CD_4 diffusion and desorption.

3.5. Consideration of features of hydrogen isotope trapping in CFC tokamak tiles

Features of the deuterium trapping in CFC N11 evaluated in this study, namely the time (flux) dependence of the deuterium retention, deuterium trapping under low-energy ion irradiation, deuterium trapping at ion/electron activated centers offer new opportunities for assessment of the hydrogen isotope trapping and retention in CFC tokamak tiles. In particular, the following considerations concerning the hydrogen retention could be done:

- To correct estimation of inventory of hydrogen isotopes in graphite tiles the parameters of tokamak tiles should be taken into account. For the same ion fluence, the deuterium retention in the CFC tiles during long-term discharges is assumed to be higher than that for short-term discharges.

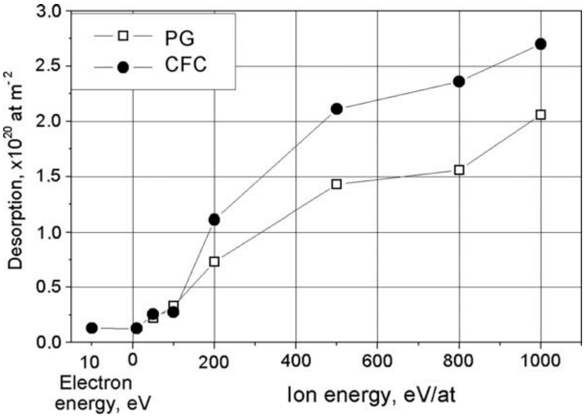

Fig. 3. Amount of deuterium desorbed as CD_4 molecules from CFC N11 and PG as a function of an energy of impinging ions or electrons (the ion flux is 1×10^{20} D/m^2 s).

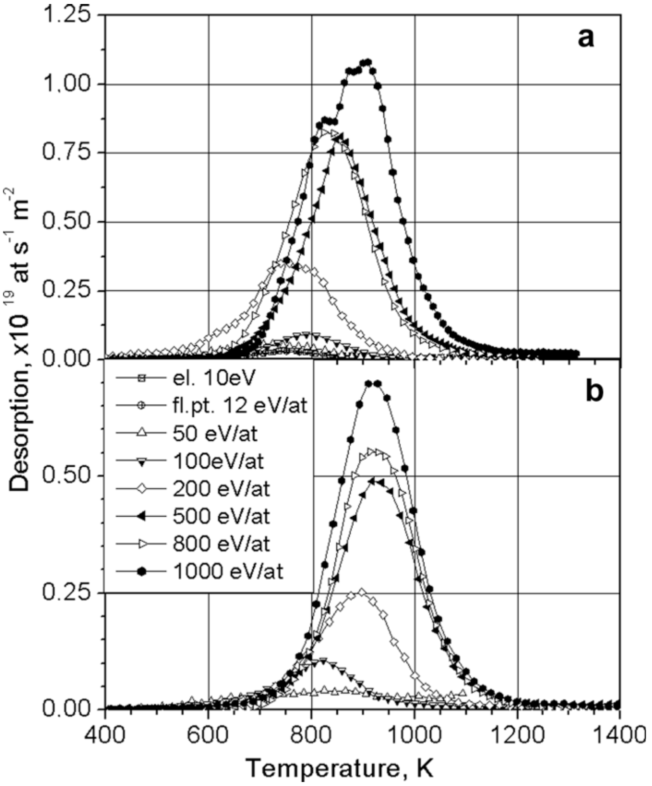

Fig. 4. Thermal desorption spectra of deuterium release as CD_4 molecules from CFC N11 (a) and PG (b) irradiated with ions at various energies and electrons (the ion flux is 1×10^{20} D/m^2 s).

- Assessment of hydrogen isotope retention is based mainly on data obtained in laboratory experiments. To get correct assessment, such conditions of the laboratory experiments as ion fluxes, duration of irradiation, hydrogen pressures in vicinity of irradiated surfaces should be considered precisely.

4. Conclusion

Deuterium trapping in CFC N11 and PG HPG99 samples irradiated with plasma ions and electron was examined with thermal desorption spectrometry. It has been found that: (1) the deuterium trapping takes place even when energy of deuterium ions approaches zero; (2) deuterium is trapped under irradiation with plasma electron and (3) for ion irradiation to equal fluences, the deuterium retention is higher at lower ion flux, i.e. the deuterium retention increases with the irradiation time.

Deuterium ions at energies above 500 eV/D are captured in the matrix bulk at traps created due to elastic collisions of energetic deuterium atoms with carbon atoms. This process may be named as 'kinetic trapping'.

Impinging electrons and ions provide creation of active centers on the surface, due to inelastic interactions with surface. These centers initiate dissociation of deuterium sorbed on the surface, penetration of D atoms into graphite and their capture. The term 'potential trapping' is proposed for this type of trapping. Potential trapping constitutes presumable part of entire deuterium trapping at energies below 200 eV/D. Under high-energy irradiation the atoms penetrating surface through potential mechanism can fill the traps formed by fast ions in the stopping zone. Time dependence of trapping in both in LEIS and in HEIS is provided by potential trapping.

In pyrolitic graphite, CD_4 molecules are not formed in the course of irradiation with deuterium ions at energies below 50 eV/D, whereas in CFC materials with high level of intrinsic defects CD_4 molecules are formed even under irradiation with deuterium ions and electrons at energy of about 10 eV. CD_4 desorption occurs, when remarkable amount of deuterium already left the surface. Porous and microchanels created at that time promote CD_4 diffusion and desorption.

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