

Long-term deuterium release from CFC NB31 in the air atmosphere

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Abstract

Long-term deuterium release from carbon fibre composite (CFC) NB31 irradiated with 200 eV D ions at room temperature to a fluence of $\sim 10^{24}$ D/m and then stored in air was investigated with the $D(^3\text{He}, p)^4\text{He}$ nuclear reaction at $^3\text{He}^+$ energies varied from 0.69 to 4.0 MeV. The decrease of retained D from the CFC NB31 with storage time was expressed by linear combination of two exponential functions of which time constants were ~ 440 and ~ 22500 hours, respectively. Accordingly, about 45 % of retained D was lost after 1-year air-storage. It has been concluded that main D loss channel is attributed to the D release from a-C:D soft layers formed on the surface and pore walls of the CFC due to re-deposition of chemically eroded hydrocarbons.

PACS. No. 52.40.Hf (Plasma-wall interactions; boundary layer effects)

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1. Introduction

Carbon fibre composites (CFCs) have been widely used as plasma-facing wall material (PFM) in current fusion devices such as JET, JT-60U, TFTR and Tore Supra, and envisaged as armour material of the divertor target plates of ITER during the non-active phase because of its favorable thermomechanical properties. There is, however, a concern that such carbon-based materials can build up the in-vessel tritium inventory due to the codeposition of eroded carbon with tritium, which can strongly affect the ITER operational schedule. In addition, it was reported that the amount of D retention in CFC continuously increases with the square root of D fluence without saturation while that in pyrolytic graphite reaches quasi-saturation above a certain amount of D fluence [1]. This is due to the D accumulation in CFC bulk, which could also enhance fuel retention in a vacuum vessel. In order to characterize the hydrogen isotope retention in fusion devices with CFC wall, in-situ analysis such as gas-balance experiment and various post-mortem analyses have been performed in major fusion devices in recent years.

In some tokamak experiments, non-negligible mismatch in results between gas-balance data (which is used for evaluating how many particles are trapped in the vessel during a discharge, sessions and so on), and post-mortem analyses (which assess the amount and location of D retention) was frequently found even allowing for the error margin of each result. Experimental observation showed the long-term D retention estimated from post-mortem analyses was normally smaller than that estimated from gas balance measurement [2]. One could consider from those results that some fraction of retained D in CFC tiles was lost during the storage after removal from the vacuum vessel. This was the motivation for an experiment to clarify the long-term behaviour of D retained in CFC material.

In this study, the release behaviour of D, which was implanted as low energy ions, from CFC was investigated under controlled laboratory condition, and the possible effects / consequences of air exposure on the D content of the samples removed from the vessel are

discussed.

2. Experimental procedure

3D CFC NB31 (density: $\rho = 1.9 \text{ g/cm}^3$, open porosity: $\sim 8 \%$) was cut with a dimension of $12 \times 15 \times 1.0 \text{ mm}^3$ with the surface-plane parallel to the needled PAN fibre bundle direction. The sample was then cleaned by ultrasonic cleaning, but no any other special pre-conditioning was done. Irradiation with D ions was performed in the High Current Ion Source at IPP-Garching. The energy and flux of the D ion beam were 600 eV D_3^+ (200 eV/D) and $\sim 3 \times 10^{19} \text{ D/m}^2$, respectively. The angle of incidence was normal to the target surface and the irradiation was carried out at room temperature without intentional heating / cooling.

After irradiation to the predefined fluence of $\sim 1.5 \times 10^{24} \text{ D/m}^2$, the sample was transferred from the High Current Ion Source to the chamber for ion beam analysis (via atmosphere), and the amount of retained D was measured by nuclear reaction analysis (NRA) using $^3\text{He}^+$ as probe beam. In this case, the concentration and amount of D retained in the sample surface can be determined by counting emitted protons produced by the $\text{D}(^3\text{He}, \text{p})^4\text{He}$ nuclear reaction. In order to analyze the D depth profile in deeper regions up to $\sim 16 \mu\text{m}$, the $^3\text{He}^+$ energy was varied from 0.69 MeV to 4.0 MeV , and the protons for each ^3He energy were counted by a wide-angle surface barrier detector at a laboratory angle of 135° . For depth profile analysis, the proton yield of an assumed depth profile as a function of incident $^3\text{He}^+$ energy was calculated by SIMNRA program [3]. The form of the assumed D depth profile was then modified and iterated until the calculated proton yield curve matched the experimental curve [4] as shown in Fig. 1 (note that the proton yield changed drastically between $t = 4282$ and $t = 8760$ hours because the solid angle of proton detector changed in between due to the installation of new detector apparatus). The total amount of D retention in the surface region was determined by integrating the D

profile over the measured depth (i.e. $\sim 16 \mu\text{m}$). Measurements were repeated for the identical sample at certain intervals: 4 hours, 6 days, 1 month, 6 months and 1 year after the D irradiation in order to obtain the time evolution of retained D. The sample was stored in air between each measurement.

At a final time of ~ 22 months after the D implantation, the D release behaviour was investigated by thermal desorption spectroscopy (TDS). The sample was heated to 1270 K with a heating ramp of 0.25 K/s at a background pressure of $\sim 10^{-7}$ Pa. For comparison, another NB31 sample was irradiated with 200 eV D ions to the same D fluence ($\sim 1.5 \times 10^{24} \text{ D/m}^2$), and TDS measurement was performed about 2 weeks after the D implantation.

Modification of the surface morphology caused by the ion implantation was investigated by scanning electron microscopy (SEM).

3. Results and discussion

Deuterium depth profiles in the CFC NB31 irradiated with 200 eV D ions, as determined by NRA, are plotted in Fig. 2. Right after the D implantation, the D profile peaked at the top surface with the concentration of ~ 20 at.%. SEM pictures (Fig. 3) shows clearly that the CFC surface was modified during the D bombardment, e.g., the structure of fiber became smoothed and small pores / fissures were plugged by carbon re-depositions. Taking into account the high near-surface D concentration, the modified layer and depositions could be regarded as so called a-C:D layers. The D profiles showed long tail into the bulk as already reported in elsewhere [1,5]. According to recent experimental findings, the apparent diffusion coefficient has no temperature dependence [5], and micro-beam NRA results indicated a distribution of D in the CFC reflecting the network of pores in the bulk [6] (large pores were still opened even after D

implantation, as seen in figure 3 (b)). Although the mechanism of this deep penetration of D in the CFC bulk is still not understood completely, such results imply that hydrogen / hydrocarbon species migrate through the pores with low activation energy during the implantation. D concentration in the near surface area (first 3-4 μm in depth) decreases clearly with the storage time while that in deeper area ($> 10 \mu\text{m}$) shows only small decrease or, in some cases, slight increase with the time. One can consider that some of D can diffuse into the bulk during the storage. However, since the error in the deeper area is relatively large, it is difficult to conclude it.

Figure 4 shows the time evolution of the D amount retained in the CFC determined by integrating the depth profile up to a depth of 16 μm . The amount of D decreased quickly within the first 2 months and more gradual afterwards. This decay curve is apparently fitted by linear combination of two exponential functions as

$$Q_D = 1.97 \times 10^{21} \exp\left(-\frac{t}{4.4 \times 10^2}\right) + 8.16 \times 10^{21} \exp\left(-\frac{t}{2.25 \times 10^4}\right),$$

where Q_D is the areal density of retained D given as D/m^2 and t is the storage time in hours. In figure 4, the D amounts in the surface area ($< 3 \mu\text{m}$) and in the bulk ($3 \mu\text{m} \sim 16 \mu\text{m}$) are shown together with the total amount. One can find that the D release with shorter time constant was only observed in the surface within 3 μm in depth. As a consequence, roughly 45 % of initially retained D was lost after 1-year air-storage.

Figure 5 shows the TDS spectra obtained from both short-term (2 weeks after the D implantation) and long-term (22 months after the D implantation) CFC samples. The spectra of D_2 molecules released from short- and long-term samples showed similar shape, i.e. the spectrum was broad in the range above 600 K, and exhibited the maximum around 1000 K. For the long-term sample, the D_2 intensity was slightly lower compared to the short-term sample over the whole temperature range. In contrast, the HD intensity for the long-term sample was

higher than that for the short-term CFC sample. The integrals of HD and D₂ TDS spectra showed that the decrease of the D amount between 2 weeks and 22 months was roughly 6 %. Even if the D release during 2 weeks after D implantation (~ 20 % of initially retained D) is taken into account, the decrease of the D amount determined by TDS is smaller than that expected by NRA result. It has been shown with spectroscopic techniques that the TDS release of HD and D₂ molecules from a-C:H(D) layer in the temperature ranges from 600 to 1000 K and >1000 K is due to the decomposition of sp³-CH(D) group and sp²-CH(D) group, respectively [7,8]. It can be expected that a part of D is trapped in relatively stable state, which is not easily desorbed. It is, therefore, reasonable that the decrease of the D amount obtained from HD and D₂ spectra was not so significant up to temperatures of 1200 K. Nevertheless, the TDS result (decrease of D₂ and increase of HD) implies that part of D (~ 6 % in this study) was replaced by H during ~ 22 months of air exposure. It is assumable that loosely bound D is desorbed with other form such as hydrocarbon species or deuterated water. In this study, unfortunately, it was impossible to evaluate the influence of such species quantitatively due to the technical limit of the experimental setup.

It is well known that the properties of a-C:H films strongly depend upon the ratio of sp³ / sp² bonded carbon together with the content of incorporated hydrogen [7-12], e.g. so-called “hard” a-C:H, which predominantly consists of sp³ hybridization, and “soft” a-C:H film which has polymer-like structure with high H content. An experimental observation shows that the D content in soft a-C:D layer also decreases with the time in the air atmosphere [13] (see figure 4) whereas almost no D was lost even after 8 years of air-storage in the case of a-C:D hard film prepared by plasma chemical vapor deposition in RF glow discharge [14]. According to Causey et al. [15], co-depositions prepared by deuterium Penning discharge showed relatively quick D release, which could be also expressed by linear combination of two exponential functions with the time constants of ~ 520 and ~ 15700 hours (figure 4). It is likely that such codeposition

contains soft a-C:D-like structure, which could contribute to the D release. The mechanism is not clear at the moment, however, interactions between the air (oxygen, water vapor etc.) and unstably trapped D or chemically reactive sp-CD group might assist D release from the soft a-C:D layer. It is known that relatively stable (hard) a-C:D layer is normally formed due to bombardment of carbon materials with energetic D ions. However, since the CFC has very rough surface and porous structure, there are many places for re-deposition of chemically eroded hydrocarbons. Main D loss channel in the CFC is attributed therefore to the release of D from such soft a-C:D layers.

From the viewpoint of post-mortem analysis of the CFC sample, the influence of the D loss in CFC plasma-facing components would be considered as follows:

- 1) For CFC tiles in erosion dominated areas: This condition is equivalent to the present experiment. Chemical eroded hydrocarbons can penetrate through pores into the bulk. From soft deposited a-C:H layers on pore surfaces D₂ and hydrocarbon molecules and radicals may diffuse out with time. As these areas do not constitute the major inventory in tokamaks, the release is not of importance for the inventory.
- 2) For CFC tile gaps: Gap deposition is the major retention process in high flux, erosion dominated areas. The vicinity of gap entrances will be still subjected to ion bombardment and somewhat heated up, resulting in hard a-C:H deposits. On the other hand, depositions formed at deeper in the gap could be partly soft layers. In this case some of D could be released during air exposure.
- 3) For CFC tiles in deposition dominated, but plasma-exposed area: It is not expected that a-C:D soft layers will be formed because of energetic ion bombardment and higher surface temperature. Such condition is favorable for the formation of hard layer. Although these areas constitute a major part of the inventory in fusion devices (TFTR, Tore Supra) the D loss from such CFC tiles during air-exposure will be not significant (a part of D atoms could

be replaced by H atoms, as it was shown in the TDS result).

- 4) For co-depositions in the shadowed areas / remote areas: Since the temperature of those area is normally low and there is almost no ion bombardment, soft a-C:D layers are likely to be formed there. In major tokamaks, the polymer-like a-C:D layers were already found in the remote areas such as divertor pump ducts [16-18]. In such case, a D loss from the co-deposits during the air-storage should be considered. Actually, such co-deposited layers collected from ASDEX Upgrade showed quick release of D with the loss rate of $\sim 0.1\%$ /day [14].

4. Summary

Long-term deuterium release from CFC NB31 irradiated with 200 eV D ions at room temperature to a fluence of $\sim 10^{24}$ D/m and then stored in the air was investigated. The decrease of retained D in the NB31 CFC was expressed by linear combination of two exponential functions of which time constants were ~ 440 and ~ 22500 hours, respectively. Accordingly, about 45 % of retained D in CFC was lost after 1-year air-storage. TDS result implied that some of D was lost due to the replacement by H during the air exposure. In general, major D loss channel in CFC is attributed to a release of loosely retained D in a-C:D soft layers formed on the surface and pore walls of the CFC due to re-deposition of chemically eroded hydrocarbons.

Acknowledgement

The authors appreciate J. Dorner, Th. Dürbeck, M. Fußeder, G. Matern and A. Weghorn for their technical assistance. One of authors, K. Sugiyama would thank the support by JSPS Postdoctoral Fellowship for research abroad.

References

- [1] Roth J, *et al.* 2007 *J. Nucl. Mater.* **363-365** 822
- [2] Brosset C, Khodja H and Tore Supra team, 2005 *J. Nucl. Mater.* **337-339** 664
- [3] Mayer M, 1997 *SIMNRA users guide, IPP report 9/113*, Max-Planck-Institut für Plasmaphysik
- [4] Alimov V Kh, Mayer M, Roth J, 2005 *Nucl. Instr. and Meth. in Phys. Res. B* **234** 169
- [5] Alimov V Kh and Roth J, 2007 *Phys. Scripta* **T128** 6
- [6] Khodja H, Brosset C and Bernier N, Nucl. 2008 *Instr. and Meth. in Phys. Res. B* **266** 1425
- [7] Biener J *et al.*, 1994 *Surf. Sci.* **307-309** 228
- [8] Th. Zecho *et al.*, 2001 *J. Phys. Chem. B* **105** 6194
- [9] von Keudell A, Jacob W, 1995 *Appl. Phys. Lett.* **66** 1322
- [10] von Keudell A, Jacob W, 1996 *J. Appl. Phys.* **79** 1092
- [11] von Keudell A, Jacob W, 1997 *J. Appl. Phys.* **81** 1531
- [12] Jacob W, 1998 *Thin Solid Films* **326** 1
- [13] Mayer M, *private communication*
- [14] Wang W, Jacob W, Roth J, 1997 *J. Nucl. Mater.* **245** 66
- [15] Causey R A, Chrisman W L and Hsu W L, 1989 *J. Vac. Sci. Technol.* **A7** 1078
- [16] N. Bekris *et al.*, 2005 *J. Nucl. Mater.* **337-339** 659
- [17] Mayer M, Rohde V and the ASDEX Upgrade team, 2006 *Nucl. Fusion* **46** 914
- [18] Masaki K *et al.*, 2007 *Nucl. Fusion* **47** 1577

Figure captions

Figure 1.

Measured (points) and calculated (lines) proton yields for assumed D profiles (see figure 2) as a function of the analyzing ^3He energy for CFC NB31 irradiated with 200 eV D ions at room temperature to a fluence of $\sim 1.5 \times 10^{24} \text{ D/m}^2$ and then stored in air for various time. Note that the solid angle of proton detector changed between $t = 4282$ ($1.57 \times 10^{-1} \text{ sr}$) and $t = 8760$ hours ($2.99 \times 10^{-2} \text{ sr}$) due to the installation of an improved detector.

Figure 2.

Deuterium depth profiles as determined by the NRA energy-scanning method in CFC NB31 irradiated with 200 eV D ions at room temperature to a fluence of $\sim 1.5 \times 10^{24} \text{ D/m}^2$ and then stored in air for times ranging from 4 to 8760 hrs.

Figure 3.

SEM images of the CFC NB31 surface before (a) and after irradiation with 200 eV D ions to a fluence of $\sim 1.5 \times 10^{24} \text{ D/m}^2$ at room temperature (b).

Figure 4.

Evolution of D amount in CFC NB31 irradiated with 200 eV D ions at room temperature to a fluence of $\sim 1.5 \times 10^{24} \text{ D/m}^2$ and then stored in air (as it was determined by integrating the D depth profiles), in soft a-C:D layer with refractive index of ~ 1.59 [13], and in co-deposition layer [15], as a function of the storage time.

Figure 5.

TDS spectra of HD and D₂ molecules released from CFC NB31 2 weeks (short-term sample) and 22 months (long-term sample) after the D implantation.

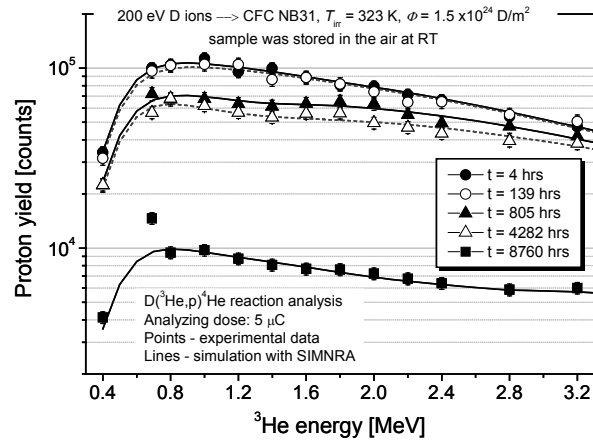


Figure 1

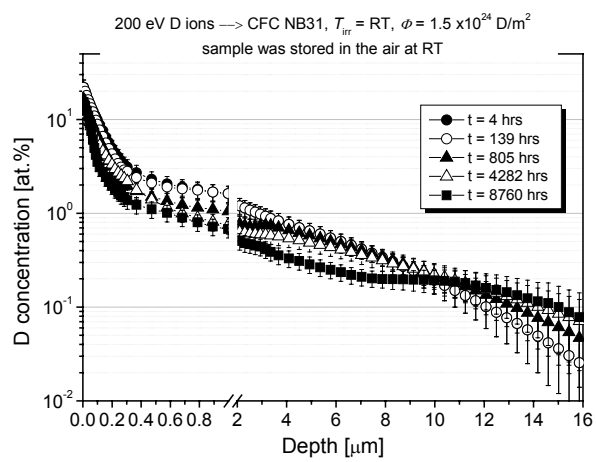


Figure 2

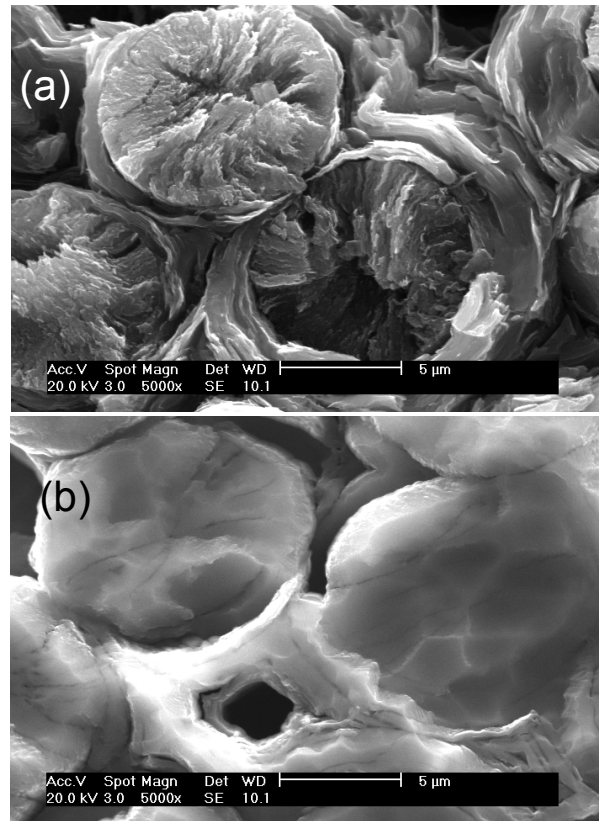


Figure 3

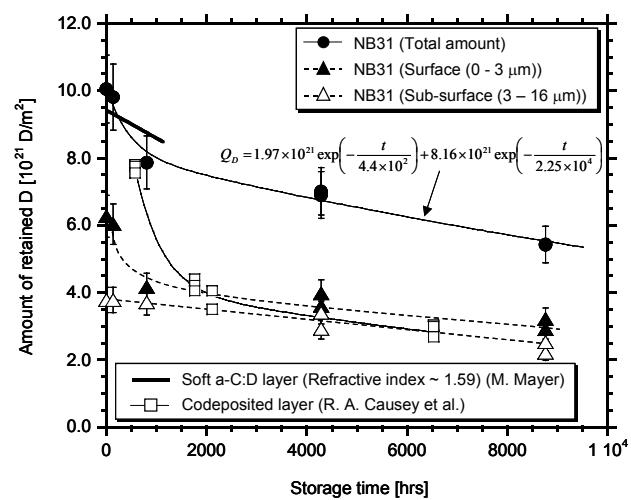


Figure 4

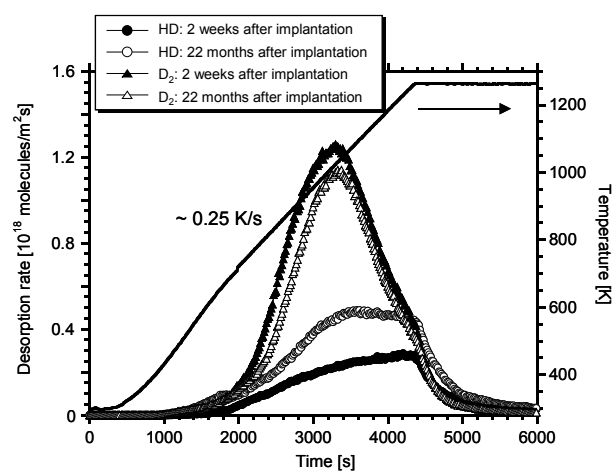


Figure 5