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Deuterium accumulation in carbon materials at high fluence

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ABSTRACT

D retention in fine grain graphite MPG-8 and carbon fiber composite NB31 after exposure to plasma was investigated by means of thermal desorption spectroscopy. It was observed, that deuterium accumulation in the two materials was similar in the region of the fluence of 10^{22}–4×10^{24} D^+/m^2, though NB31 retains about twice as much. The retention in MPG-8 reveals no saturation at high fluences and no flux dependence in the range of $(0.5–3.5) \times 10^{20}$ D^+/m^2 s. The difference between polished and unpolished samples, as well as between samples kept in air for various times after irradiation was within the experimental uncertainty.

1. Introduction

Tritium retention in carbon-based materials is known to be a point of concern in fusion devices. There were many experiments on hydrogen trapping and release with various types of carbon materials. Many of accumulation experiments were made with energetic ions in the region of 1–20 keV [1–7]. There are also experiments with plasma irradiation [8–13], and the spread between them is rather high. This may be due to various factors, including the difference in experimental conditions. This work is devoted to investigations of deuterium trapping in fine grain graphite MPG-8 and carbon fiber composite NB31 in various conditions at the fluence in the range of 10^{22} to 10^{24} D^+/m^2.

2. Thermal desorption spectroscopy facility

An ultra high vacuum stand was designed for thermal desorption spectroscopy (TDS) experiments. The scheme of the facility is shown in Fig. 1. The main components of the vacuum system are: the main chamber with a volume (V_1) of 4.1 l, a turbomolecular pump TMU-071 (with a dry scroll pump VARIAN SH100) and an ion-getter pump (for night pumping) each attached through valves, calibration system, a quadrupole mass spectrometer (QMS) PFEIFFER-VACUUM QMS-200 M1. The main chamber is connected through a gate valve with a sample loading chamber with another turbomolecular pump and a liquid nitrogen trap. The carbon samples are mounted on two thermocouple wires, which are mounted on the bar of a linear feedthrough that can move the sample between the loading chamber into the main chamber through the gate valve.

The residual gas pressure in the main chamber is less than 1.3×10^{-9} mbar after baking with hydrogen (H_2) to be the main component and less than 1.3×10^{-8} mbar after loading the sample. An additional sealing of the gate throat between the chambers was used after moving the sample into the main chamber. The sample was heated by radiation from a resistive U-shaped W strip surrounding the sample. The sample was heated linearly with the rate of 2 K/s to the maximum temperature of 1600–1700 K.

The experimental procedure consists of the following steps. The main chamber was baked at 200 °C for 50 h, while the sample was kept in the loading chamber at room temperature at 10^{-7} mbar. Then the main chamber was cooled down to RT. The ultimate pressure was 10^{-9} mbar. Then the target heater (W strip) was heated at its maximum temperature for 5 min and cooled down. Then, the loading gate valve was opened and the sample was moved into the heating region and linearly heated for TDS measurements.

Pre-heating of the W strip permitted to reduce the gas release from surrounding surfaces to a negligible level, only small desorption of H_2, H_2O, and CO was observed. No background increase was observed in evolution of the deuterium containing species (the partial pressures at 1600 K were about the same as before heating). No release of D containing gases was detected in control runs after TDS measurements. Reactions between released molecules could take place on the hot tungsten heater giving uncertainty in interpretation of the molecular composition of gas released from the sample.

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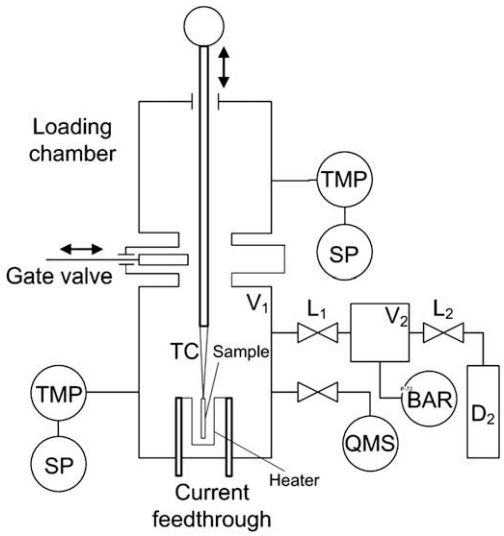

Fig. 1. The scheme of the TDS facility. SP, scroll forevacuum pump; TMP, turbomolecular pump; TC, thermocouple; BAR, baratron; L_1 and L_2, leak valves.

3. Calibration

Measurements of TDS were performed in the constantly pumped vacuum volume (V_1). If the pumping speed (S) is high, the gas release rate (q) is proportional to the gas pressure (p) increase: $q = k_1 S_p$, where k_1 is a constant.

If QMS signal I_{QMS} is proportional to the pressure ($p = k_2 I$), then $q = k_1 k_2 S I_{QMS}$. The coefficient $k_q S$ was determined through a calibration procedure with a usage of a small calibration volume $V_2 \ll V_1$ with two leak valves L_1 and L_2, shown in Fig. 1. If L_1 is closed and L_2 opened, the leak rate in V_2 is measured by a capacitance gauge BARATRON: $q_0 = k_1 V_2 dp/dt$. If L_1 is opened, the deuterium leak rate and QMS signal I_{QMS} are connected: from these two measurements, we find that $k_q S = (V_2/I_{QMS})(dp/dt)$.

The coefficients $k_q S$ measured in this way for H_2 and D_2, were 4.4×10^5 and 10^6 l mbar/A s, respectively.

The coefficient $k_q S$ for HD was found using another procedure. For this purpose, TDS of D_2 and HD from a tantalum sample irradiated by D ions to a certain fluence were measured. Tantalum is known to trap all implanted deuterium ions [14]. Therefore, the number of deuterons in TDS of D_2 and HD molecules equals to the number of implanted deuterons. It was found in this way that $(k_q S)_{HD} = 0.5(k_q S)_{D2}$.

Though this value was used in experiments, it seems to be underestimated as it is only slightly higher than $(k_q S)_{H2}$. Therefore, one can expect that D release in TDS was slightly underestimated. Further analysis of calibration is necessary.

4. Experimental

Samples, made of fine grain graphite MPG-8 (NII GRAPHIT, Russia), the density is 1.85 g/cm^3) and carbon fiber composite NB31 (SEP, Bordeaux, France, 1.9 g/cm^3) with dimensions $10 \times 10 \times 1$ mm were used in the experiments. A number of MPG-8 samples were polished mechanically, cleaned in an ultrasonic bath and then degassed in vacuum 2×10^{-5} mbar at 1200 °C for 15 min. All NB31 samples remained unpolished, as well as some of the MPG-8 samples.

Implantation of deuterium was performed using radio frequency (RF) plasma discharge [15] and the beam plasma discharge [16]. Also, a mass-separated 10 keV D_3^+ ion beam was used.

Parameters of RF plasma discharge were: the ion energy 300 eV (100 eV/D$^+$ for the main component D_3^+), the ion flux 1.4–2.6×10^{20} D$^+$/m^2 s, the sample temperature 90–150 °C, and the deuterium pressure 6.7×10^{-4} mbar. Parameters of beam plasma discharge were the ion energy 200 eV (mainly D$^+$), the ion flux 2.6×10^{21} D$^+$/m^2 s, and the sample temperature below 50 °C. The energy of the mass-separated ion beam was 5 keV/D$^+$ (10 keV/D_2^+), and the sample temperature was about 20 °C.

Mass spectra of ions in RF plasma discharges and beam plasma discharges were not controlled in every experiment and this can be the reason of the uncertainty of the flux measurements.

5. Results

The typical spectra of D_2 release after RF plasma irradiation of MPG-8 and NB31 are shown in Figs. 2 and 3. One can see, that deuterium desorbs in a very wide temperature range – from 400 K to 1400 K with a maximum release rate around 800 K. The shapes of the spectra are similar for both materials. One can distinguish three peaks: 500 K, 750–800 K, and 1100–1400 K. Tentative analyses leads to the suggestion that each peak consists of several very narrow peaks. The peak at 750–800 K always dominates at high fluence. Though the spectra are similar, there are some differences in relative amplitudes of the peaks. The D_2 release rate is two times higher for NB31.

Deuterium releases also in the form of HD, HDO and CD_4. Fig. 4 shows an example of TDS measurements of masses 3 (HD), 4 (D_2), 19 (HDO) and 20 (CD_4) from NB31. The positions of peaks in spectra of HD and D_2 always correlate. HD signal can be connected with H_2 release and subsequent recombination on hot surfaces (sample, heater, QMS cathode). The high temperature (>1200–1300 K) part of HD spectra can be connected with rapid increase of H_2 release from walls at high temperature, which was usually observed.

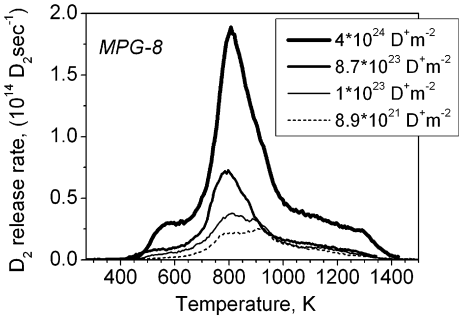

Fig. 2. Release rate of D_2 from MPG-8 after irradiation in RF plasma discharge at room temperature to various fluences.

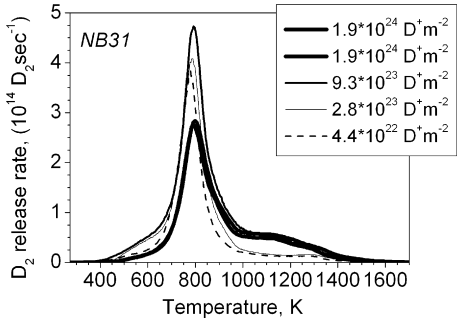

Fig. 3. Release rate of D_2 from NB31 after irradiation in RF plasma discharge at room temperature to various fluences.

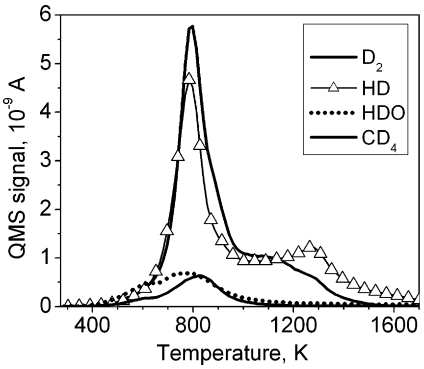

Fig. 4. An example of TDS of D_2, HD, HDO, and CD_4 from NB31 after irradiation in RF plasma discharge at room temperature to the fluence of 1.9×10^{24} D^+/m^2.

Controlled experiments with tungsten sample, which contains small amounts of H_2 and H_2O, demonstrated that release of H_2 and H_2O was always small at $T < 1200$–1300 K and high at $T > 1200$–1300 K. Therefore release of HD and HDO from carbon materials at $T < 1200$–1300 K can be connected with hydrogen and water absorbed in the samples.

Release of CD_4 is peaked around 800–850 K (Fig. 4), consistent with experiments on deuterium plasma ions exposure [10,12]. The total amount of CD_4 release is an order of magnitude less than that of D_2. Release of C_2D_5 is two orders of magnitude less than that of CD_4. This allows us to expect a small error in calculation of the total D retention as the sum of D_2 and HD molecules, without taking into account deuterocarbons.

6. Deuterium trapping

Fig. 5 represents the dependence of deuterium trapped on the fluence calculated from TDS.

First, the calibration was tested by using a tantalum irradiated by 10 keV D_2^+ ions (crosses in Fig. 5). One can see that the results fit well to the 100% trapping in tantalum [14]. Another test was made with implantation of 10 keV D_2 ions in graphite. The retention is of about 100% at the low fluence and 'saturates' at the fluences above 2×10^{21} D^+/m^2 in Fig. 5. Qualitatively this is in agreement with other observations [1–7].

The results of our measurements for MPG-8 (triangles with thick edges) and NB31 (squares) after RF plasma discharge and beam plasma discharge irradiation are shown in Fig. 5. The total

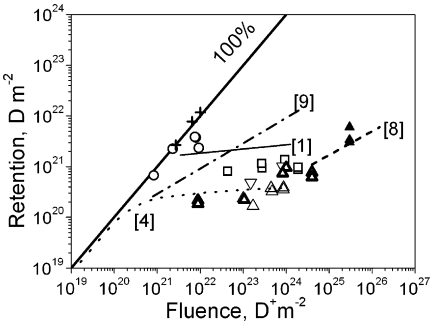

Fig. 5. Fluence dependence of deuterium retention in carbon-based materials: MPG-8 irradiated in RF plasma discharge (triangles with thick edges – irradiation of polished side, inversed triangles – irradiation of unpolished side, triangles with thin edges – the samples kept in air for 2–15 days after irradiation), MPG-8 irradiated in beam plasma discharge (filled triangles), NB31 irradiated in RF plasma discharge (squares), MPG-8 irradiated by ion beam (circles), tantalum samples irradiated by ion beam (crosses). The experimental uncertainty of TDS measurements is within 30%. The lines are taken from Refs. [1,4,8,9].

trapping in NB31 and MPG-8 increases with the ion fluence without saturation. The retention in NB31 is slightly higher, than that in MPG-8. Samples irradiated in beam plasma discharge to the higher fluence of 3×10^{25} D/m^2 demonstrated further increase of retention (filled triangles in Fig. 5). It is important to conclude from these measurements that trapping does not saturate at the high fluence not only in CFCs but also in powder graphites.

Fig. 5 shows also approximations of experimental points taken from Refs. [8,9], which were obtained after implantation of 200 eV mass-separated D^+ ions in NB31 and after implantation of 150 eV ions from plasma in PISCES-A in N11, respectively. The results differ by an order of magnitude. Our measurements are closer to those given in [8].

To check possible influence of the sample preparation, several additional measurements have been performed.

Some of MPG-8 samples were polished mechanically, but some samples (inversed triangles in Fig. 5) were unpolished. It was concluded, that surface polishing does not influence the amount of trapped deuterium within the experimental uncertainty. The shapes of the spectra from polished and unpolished samples were also similar.

TDS measurements are usually made not immediately after plasma irradiation. Possible influence of keeping in air for 2–15 days after irradiation was also investigated. The conclusion was that keeping in air (triangles with thin edges in Fig. 5) does not lead to remarkable release of trapped deuterium. This conclusion agrees with [10].

Variation of the ion flux density in the range of $(0.5$–$3.5) \times 10^{20}$ D^+/m^2 s for the fluence of 4.5×10^{23} D^+/m^2 demonstrated that there were no obvious tendencies both of TDS variation and deuterium retention. Experiments [2] with high-energy D ion beam also showed no dependence of retention in pyrolytic, pseudo-monocrystal, and fine grain graphite on the ion flux density in the range of 10^{18}–10^{21} D^+/m^2 s.

One must mention an important observation. Measurements of TDS spectra were usually reproducible. Nevertheless, TDS, which did not correlate with other spectra, and even TDS, which differ drastically from other spectra, were sometimes observed. Once we observed unpredictable difference even in the case several samples were irradiated simultaneously. These observations demonstrate that plasma irradiation is not as well controlled instrument in comparison with the ion irradiation. Plasma parameters are not always well defined and predictable. Variable ion composition, hot atoms and molecular gas may influence measurements. Secondary ion-electron emission can not be taken into account in plasma irradiation experiments. This is why the spread from experiment to experiment that is seen in publications as well as the spread between the results obtained in different laboratories can be rather large even if other conditions of the experiment are supposed to be the same.

7. Conclusion

A new ultra high vacuum stand was assembled for thermal desorption experiments. The release of gases from surrounding materials was reduced to minimum, so that deuterium release only from the sample was monitored.

Thermal desorption of deuterium implanted at 50–100 °C in fine grain powder graphite MPG-8 and carbon fiber composite NB31 was investigated. TDS lie in a wide range of temperatures from 400 K to 1500 K and consist of several peaks. The peak with maximum at 800 K dominates in all spectra at high fluences. Desorption takes place mainly as D_2, HD, HDO and CD_4. Release of D_2 and HD are similar in rate. Release of HDO and CD_4 was always one order magnitude less, than that for D_2.

Trapping of deuterium as a function of fluence was measured up to the fluence of 3×10^{25} D^+/m^2. No saturation with the fluence was observed not only for NB31 but also for MPG-8. In general, NB31 traps twice as more deuterium as MPG-8. Trapping at various ion fluxes did not demonstrate a flux dependence. Samples with polished and sawed surfaces gave similar trapping. Keeping in air after irradiation for 2–15 days showed very similar results.

It was concluded that experiments on plasma irradiation are not well controlled if to compare with experiments on ion implantation, and this may give rise to the spread in the experimental data that is often observed in literature.

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