Hydrogen retention in volumetric CFC structures

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Abstract. The paper experimentally investigates and analyses the features and mechanisms of both of oxygen removal by deuterium glow discharge from CFC, pyrolytic graphite and stainless steel subjected to irradiation in oxygen contaminated plasma. It is shown that oxygen implanted in PG perpendicular to basal plates is removed after sputtering the layer slightly thicker than oxygen stopping zone (≈2nm). Fast deuterium ions penetrating into CFC during GDC transfer the trapped oxygen atoms into the bulk. Thus, much thicker surface layer has to be removed (500-1000 nm) for oxygen release.

1. Introduction
Oxygen impurity presented in plasma of fusion devices leads to a number of negative effects. Among them there are parasitic radiative power, delution of fuel particles, accelerated erosion rate of plasma facing materials, enhanced trapping and recycling of fuel particles.

Various types of discharges providing irradiation of plasma facing materials with weakly ionized plasma (glow discharge, rf-discharge, Taylor discharge) are routinely used for removal of oxygen and other impurities from the first walls of today tokamaks. Nevertheless the mechanisms of oxygen release from the ion irradiated metal and graphite are not understood satisfactorily. Its detail investigation seems to allow optimization of conditioning process.

The paper is devoted to the results of experimental investigation of oxygen (O) removal by deuterium (D) glow discharge (D₂-GDC) from carbo fiber composite (CFC), pyrolytic graphite (PG) and stainless steel (SS). Parameters, peculiarities and mechanisms of O release by D₂-GDC from CFC and PG irradiated in O contaminated plasma are presented.

The experiments were performed in the electron initiated discharges. Parameters of irradiating ion flux were rather close to those of glow discharge. Thus, we use the term GDC for surface cleaning process realized in this study.

2. Experimental
The experiments with CFC samples were performed in the thermal desorption stand – (TDS-1, figure1) presented earlier [1]. The main feature of the TDS-1 is a possibility to irradiate the samples in the gas discharge ignited in the plasma chamber of the stand, and to make a thermal desorional analysis of the samples in the same plasma chamber.
The sample heating rate during TDS measurements was equal to 5 K/s. For an absolute calibration of the mass-spectrometer, a gas output from the implanted sample was modeled by the gas flow into the plasma chamber through a calibrated leakage.

![Figure 1. Thermal Desorption Stand (TDS-1). 1 – Heated cathode, 2 – Sample heater, 3 – Sample, 4 – anode, 5 – Monopole mass-spectrometer, 6 – Water-cooled plasma chamber, 7 – Plasma, 8 – Puff in, 9 – Vacuum vessel, 10 – Pipe line.](image)

### 3. Sample treatment and experimental procedure

The samples of CFC N11 and pyrolytic graphite were used for experiments. After machining they were washed in ultrasonic bath and annealed. The CFC samples were annealed at 1800 K for 5 minutes and SS samples at 1450 K for 5 minutes.

Each experimental cycle included sample annealing, irradiation in (D₂ + 2%O₂)–plasma and irradiation in D₂–plasma (GDC). (D₂ + 2%O₂)–plasma was selected for the experiments, because such composition of plasma in our experimental conditions provided maximum O trapping practically not depending on accidental variation of O concentration [2]. Irradiation in (D₂ + 2%O₂)–plasma was performed under the following conditions. Ion energy \( E_i = 100 \text{ eV/at} \) (for SS samples), \( E_i = 100 \) and 400 eV/at (for CFC samples), ion flux \( j_i = 1 \times 10^{20} \text{ at/m}^2\text{s} \), fluence \( \Phi_i = 5 \times 10^{23} \text{ at/m}^2 \), sample temperature \( T = 450 \text{ K} \). For GDC it was \( E_{\text{GDC}} = 100 \) and 400 eV/at, \( j_{\text{GDC}} = 2 \times 10^{19} \text{ at/m}^2\text{s} \), \( T = 450 \text{ K} \). The experimental series with CFC samples are indicated as 100/100, 100/400, 400/100 and 400/400 combinations.

For determination GDC efficiency, the cycles were made with different GDC duration, and after each cycle an amount of oxygen remained in the sample was measured by TDS.

During TDS examination oxygen was released from CFC samples mainly in the form of CO (99%) and minor portion as CO₂ (1%). That is why the paper considers only CO release.

### 4. Experimental results and discussions

Oxygen was practically totally removed from PG samples, when surface layer slightly thicker than O stopping range (inset at figure 2) was sputtered (figure 2). Contrary to that, removal of 50 nm thick layers caused only small decrease of O retention in CFC samples (figure 2). Further sputtering led to decrease of O content in the samples with practically constant rate.

In all cases almost total release of O was observed after sputtering the layers many times exceeding O and D ion stopping ranges. The thicker layer (≥1000 nm) was to be sputtered and the shortest time (900–100 min) was needed for O release with 400 eV GDC (combinations 100/400 and 400/400), and vice versa for the combinations 400/100 and 100/100 the thickness 500–600 nm was supposed to be sputtered during 150–200 min. Sample temperature did not influence remarkable the rate of GDC (figures 2 and 3).

It could be assumed that penetration of O into the bulk occurred due to diffusion of implanted O atoms, or due to filling of internal pores with O atoms during implantation in (D₂ + 2%O₂)–plasma.
But in such cases O release rate during GDC in contradiction with experimental results should not depend on energy of impinging D ions, should not be constant but should be independent of the sample temperature.

Figure 2. CO desorption from CFC and PG via thickness of sputtered away layers during GDC. Experimental series: ■ – PG 400/400 at 200°C, CFC: ● – 100/100 at 120°C, ▲ – 400/400 at 200°C, ○ – 100/400 at 200°C, □ – 400/100 at 200°C, △ – 100/100 at 200°C. The inset shows depth distributions of deuterium and oxygen ions implanting graphite with 100 and 400 eV energies. (Calculation is made with SCATTER code [2], black line – D⁺ 100eV, black dots D⁺ 400eV, gray line O⁻ 100 eV, gray dots O⁻ 400 eV)

Figure 3. CO desorption from CFC via GDC duration: ■ – 100/100 at 120°C, ● – 400/400 at 200°C, ▲ – 100/400 at 200°C, ▼ – 400/100 at 200°C, ○ – 100/100 at 200°C, △ – implantation j=2x10¹⁵ at/cm², ◀ – GDC j=2x10¹⁵ at/cm²

We believe that O was transferred into the bulk due to collision cascades originated by fast D ions during GDC. For ion energies used in our experiments the mean energy of primary recoils (T) could be determined as \( T = \frac{1}{2}E_D[4M_D M_C/(M_D+M_C)^2] \), where \( E_D \) and \( M_D \) are energy and mass of deuterons,
and M is mass of target atoms. The value of T is 25 eV, when \( E_D = 100 \text{ eV} \), and \( T \approx 100 \text{ eV} \), when \( E_D = 400 \text{eV} \).

Each D atom impinging CFC surface with energy 100 eV can displace 4–5 atoms in average, and at least 11–16 atoms can be knocked out and transferred by 400 eV atom. It means that the rate of O atom transfer into deep layers was much higher, than the rate of their release from the surface layers sputtered by D ions with energies 100–400 eV. As a result O was accumulated mainly in the region of ion penetration, the surface layers appeared to be depleted of O, its emission due to surface sputtering was slowed down, and thicker layer needed to be sputtered for total oxygen removal.

The constant rate of O release indicates that O depth distribution in the near surface layers was constant during main part of GDC. It can be provided, if O concentration in permanently transferred “accumulating” layer stayed without changes during main part of GDC. More probably, O concentration in this layer was kept at saturation level, but its thickness thinned down along with the time. As soon as the layer had been exhausted GDC was finished.

The smaller rate of O removal at the first stage of GDC shows that O concentration in the near surface layers was smaller than those at the later stages. The reason of that could be a redistribution of O atoms in D stopping zone after finishing of \( D_2 + 2\%O_2 \) plasma irradiation and starting of GDC.

The ratio of sputtering yields for D ions with energies 400 eV and 100 eV equals \( Y_{400eV}/Y_{100eV} \approx 1.5–1.6 \). This value is smaller than the ratio of the numbers of O atoms displaced by ions of these energies \( N_{400}/N_{100} \approx 4 \). Thus O concentration in the sputtered surface layers appeared to be higher under 100 eV GDC, and accordingly, higher O amount was released with each sputtered carbon layer. That is why, thinner surface layer should be sputtered away by 100 eV GDC for O removal, than by 400 eV GDC.

Additional reason of lower O concentration in the sputtered layers during 400 eV GDC is radiation induced surface stresses. 400 eV ion irradiation results in formation of higher compress stresses in stopping zone and accordingly in higher tensile stresses in the underneath layers. It may cause easier O penetration (as well as D penetration) from stopping zone into the bulk layers, decrease of O concentration in near surface layers and finally slowing down the rate of O removal.

Different O distribution and concentration in dependence on energy of implanting ions have been established in the near surface layers during \( (D_2 + 2\%O_2) \)-plasma irradiation. That is why at the first stage of GDC the O retention in 100/400 combination decreased at the same way as in 100/100 combination (figure 2). In a while O distribution in CFC was “reconstructed” under 400 eV D ion irradiation, and further O removal in 100/400 and 400/400 combinations were similar.

Fast O removal from PG samples can be explained by strong dependence of particle displacement on graphite structure orientation. One can believe that displacement is negligibly small in directions perpendicular to graphite hexagonal plates and reaches maximum in direction parallel to them. This fact accounts for high O displacement along with the axis of CFC fibers, when the fibers are oriented perpendicular to irradiating surface.

5. Summary

The paper presents results of experimental investigation of oxygen removal by deuterium D-GDC from CFC N11 and pyrolytic graphite PG99.

Oxygen was removed from PG implanted perpendicular to its basal plates after sputtering the layer slightly thicker than D stopping zone (≈ 2 nm). It was necessary to sputter much thicker layer and to spend more time for O removal from CFC. It is ≈1000 nm and \( t \approx 90 \text{ min} \), if \( E_{GDC} = 400 \text{ eV/at} \), and ≈ 500 nm and \( t \approx 200 \text{ min} \), if \( E_{GDC} = 100 \text{ eV/at} \). The results were explained by active O transfer into the bulk of CFC due to participation in collision cascades generated by fast D ions. Increase of surface temperature from 393 to 473 K did not influence the rate of GDC. It is concluded that GDC duration could be decreased down to ≈ 50 min, if ≈ 200 eV D ions is used.

The minimum of oxygen retention during D-GDC was achieved, when predominated part of O saturated barrier layer had been removed. After sputtering the barrier layer away O penetrated up to
and trapped in significantly deeper region. Oxygen trapping at this stage, more probably, occurred through potential mechanism from the water molecules absorbed at the surface.

100 eV D-GDC is preferable for SS conditioning. Oxygen retention in minimum is expected to be less, if temperature is higher and O concentration in residual gas is lower.

References
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