Chemical erosion of DIII-D divertor tile specimens

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Abstract

Chemical erosion measurements have been performed on graphite tile specimens taken from the upper and lower divertors of the DIII-D tokamak. Measurements for 50 eV/D$^+$ incident on the *lower divertor* resulted in erosion yields which are the same as those for graphite. This implies that any deposited film on the tile surface was completely removed after very short beam exposures ($\sim 10^{21}$ D$^+$/m^2). For the *upper divertor* tiles, the measured erosion yields for 50 and 200 eV/D$^+$ were somewhat larger than those for graphite at 300 and 500 K; however, at 700 K the yields were lower than graphite yields and were more comparable to boron-doped graphite.

Thermo-oxidation of both upper and lower divertor specimens also indicated the rapid removal of surface films, followed by the slower removal of implanted deuterium from the graphite substrate.
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1. Introduction

Due to its low atomic number and excellent thermo-mechanical properties, carbon in the form of graphite is extensively used as a plasma-facing material in current fusion experiments. Carbon, however, has the disadvantage of being susceptible to chemical reactions which may lead to the erosion of the material in a hydrogen plasma environment. In an attempt to improve tokamak plasma performance through the reduction of impurity influx, surface modification techniques, such as boronization, are being used in current devices, e.g., DIII-D [1].

A comprehensive spectroscopic study of carbon sources and core plasma C impurity content in DIII-D has shown that Y_{chem} at the lower divertor has decreased by a factor of ~ 10 over the 1993–2000 period of operation [2]. During this period, ~ 30 boronizations of 100–150 nm each have been performed, resulting in an average cumulative boron layer of 3–5 μm. Despite the apparent reduction in Y_{chem} from the lower divertor, there has been no significant change in chemical erosion yields from the outer midplane, which remains comparable to that of pure graphite [2], and the core carbon content has remained roughly constant [2]. However, in the region of the outer midplane, the ion flux is not considered to be sufficiently high to remove the deposited boron, and consequently the midplane was not expected to be a significant source of carbon. In order to explore these apparently contradictory results, specimens from the *lower* and *upper divertors*, as well as from the *outer midplane* were obtained, and controlled laboratory chemical erosion experiments were performed. In a previous study [3], the chemical erosion yield of *midplane* tile specimens was found to be initially comparable to that of graphite, but was seen to decrease with D$^+$ fluence. Surface analysis indicated the presence of a carbon-rich layer on top of the largely boron film created by the boronizations. We interpret the results as indicating either the deposition of C on tiles at the outer midplane, or the segregation of carbon atoms to the

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surface of the boron rich film. (Carbon makes up about 5–10% of the boronization layers [1].) In either case, the end result is an effective carbon surface facing the plasma, in agreement with the spectroscopic measurements in DIII-D [2]. Here we report on laboratory chemical erosion results for specimens obtained from the *upper* and *lower divertors* of DIII-D.

2. Experiment

2.1. DIII-D divertor tile specimens

Two specimens from the DIII-D tokamak were investigated: (1) B3 from the lower (inner) divertor, and (2) UD4 from the upper divertor. Both specimens were UCAR-TS-1792 (ATJ) graphite, and were present in the tokamak through the 1993–2000 operational period. The lower divertor specimen was located in row 2 of the DIII-D divertor floor (second row outboard of the 45° tiles around the centre column, see Fig. 1), which is usually in the private flux region, but is exposed to a mixture of plasmas. The upper divertor specimen is from row 2 of the upper divertor. Prior to D^+ or O_2 exposure in our laboratory, a series of surface analyses were performed: (1) scanning electron microscopy (SEM), (2) energy dispersive X-ray spectroscopy (EDX), (3) X-ray photoelectron spectroscopy (XPS), and (4) in the case of B3 from the lower divertor, Rutherford backscattering analysis (RBS). EDX and RBS both provide compositional information, EDX over a depth of $\sim$2–3 μm, and RBS in the near surface ($\sim$200 nm). XPS provides compositional as well as bonding information over a depth of a few nm.

2.1.1. Surface analysis of upper divertor specimen UD4

The upper divertor specimen UD4 was grey, and had the appearance of a typical plasma-deposited film. Tiny crystals ($\sim$0.1 mm) were visually observable and are clearly seen in the SEM photograph in Fig. 2(a). EDX of these crystals showed almost exclusively oxygen, with a very small amount of carbon (The EDX system was not capable of detecting boron or deuterium). The crystals
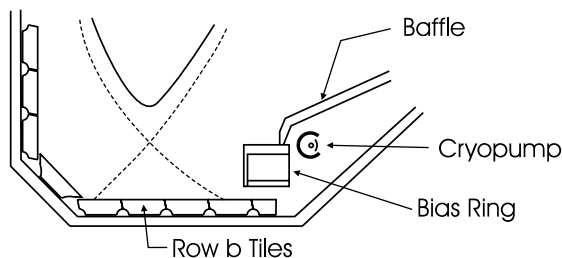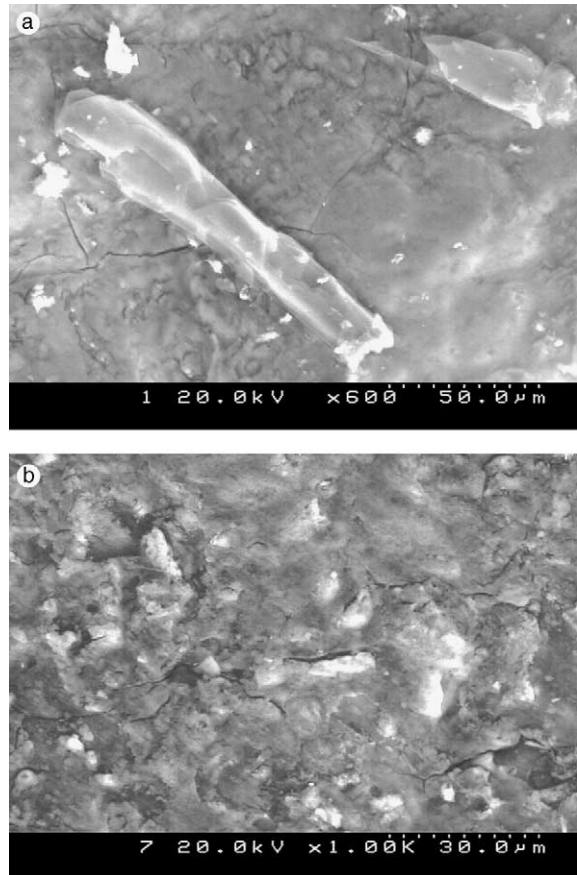

Fig. 2. SEM photograph of the surface of (a) the upper divertor tile specimen UD4, and (b) the lower divertor specimen B3. Large crystal structures are clearly visible imbedded in the underlying plasma-deposited film on UD4. A uniform and cracked surface is visible on B3.

have been identified, by Raman backscattering, as boric acid ($B–(OH)_3$), and they are thought to form upon exposure of the boron film to moisture in the air [4].

SEM of the remainder of the film showed a typical cracked-looking plasma-deposited film. EDX analysis showed the film to be primarily carbon within the first 2–3 μm, with a few at.% oxygen and a very small contribution ($<$0.5 at.%) of metals and other impurities.

XPS analyses, performed on the surface layer, and at depths of $\approx$10 $\pm$ 5 nm and $\approx$45 $\pm$ 15 nm, reveal (Table 1) a primarily carbon surface. Oxygen and boron are also present in the film, with most of the oxygen residing on the surface. The B/C ratio is seen to decrease slightly with depth but the boron content is roughly constant ($\approx$10–13%) up to 45 nm depth. Unfortunately, the XPS measurements could not separate the boron content of the crystals from the boron content of the film. However, with the crystals accounting for less than a few

Fig. 1. Schematic of the DIII-D lower divertor floor. The location of Row 'b' tiles is indicated.

Table 1
Surface composition of DIII-D upper and lower divertor tile specimens by XPS analysis

Specimen	Analysis location	B (at.%)	C (at.%)	O (at.%)	N (at.%)	B/C
UD4 (*upper divertor*)	Front surface	10	64	26	1.0	0.15
	Depth $\sim$10 nm	13	75	11	0.9	0.18
	Depth $\sim$45 nm	10	82	8	0.8	0.12
B3 (*lower divertor*)	Front surface	3.0	77.4	17.3	2.3	0.040
	Depth $\sim$5 nm	1.4	92.1	5.4	1.2	0.015

percent of the tile surface area, it is likely that the B/C ratio of 10–13% is reasonably representative of the film.

In summary, for the upper divertor specimen UD4, we have found a boron-containing carbon film, with a thickness greater than about 50 nm and B content of $\sim$10 at.%. We note that this concentration of boron has been found to reduce the chemical erosion yield of boron-doped graphites [5,6].

2.1.2. Surface analysis of lower divertor specimen B3

Specimen B3 had a blueish-grey hue and was streaked with arc tracks. SEM photographs revealed a uniform and cracked surface, which is typical for a plasma deposited film (see Fig. 2(b)). The EDX spectra show primarily carbon within the analysis zone (2–3 μm). There is $\sim$1–2 at.% oxygen, as well as trace impurities. This is consistent with an area of net erosion (primarily carbon), with evidence of some redeposition (i.e., evidence of small B concentrations, see below).

XPS analysis (Table 1) shows that the surface is composed almost exclusively of carbon, with a small amount of boron ($\approx$3 at.%) which is further reduced by 50% after a very short sputter, reaching $\sim$5 nm depth. RBS also showed that, averaged over a depth of $\sim$200 nm, the surface is primarily carbon, consistent with EDX and XPS. Although the exact film thickness cannot be deduced, it is estimated to be $\gtrsim$5 nm based on XPS.

2.2. Chemical erosion due to D^+ impact

All chemical erosion experiments of the DIII-D tile specimens were performed in the mass-analyzed low-energy ion gun facility described in [7]. The erosion experiments were conducted at selected 50 and 200 eV/D^+ ion energies and specimen temperatures of 300–700 K, approximating a broad range of operating conditions found in the DIII-D tokamak. The temperature was measured by optical pyrometry. Mass selected D_2^+ ions bombarded the target at normal incidence with a flux of 1–1.5×10^{18} D^+/m^2 s over an elliptical spot of $\approx 4 \times 6$ mm ($\approx$20 mm^2 area). (Note that D^+ is used to designate incident particles, even though the atoms in the D_2^+ molecular ions may not be ionized.) Each temperature/energy erosion case was conducted on a new spot on the specimen, and in order to minimize the changes in the

film due to heating, experiments at 700 K were the last to be performed. The hydrocarbon products of chemical erosion (CD_4, C_2D_2, C_2D_4, C_2D_6, C_3D_6, and C_3D_8) were measured in the residual gas by an ExtraNuclear quadrupole mass spectrometer (QMS), which was calibrated in situ with known leaks of CD_4, C_2D_4, and C_3D_6. The relative sensitivities of C_2D_2, C_2D_6, and C_3D_8 were estimated from previous calibrations [7]. More details of the experimental procedures are found in [7].

2.3. Thermo-oxidation of divertor tiles in O_2

Oxygen gas exposure experiments were performed in a bakeable vacuum system by backfilling the vacuum chamber with oxygen to $\sim$2.1 kPa pressure and following the methodology used in [8]. External heaters were used to heat the whole spherical exposure/desorption chamber to the desired test temperatures of 523 and 623 K, measured by two copper–constantan thermocouples attached to flanges near the specimen holder.

Subsequent to the oxygen exposure, the vacuum chamber containing the specimens was evacuated to a base pressure of $<10^{-6}$ Pa prior to laser desorption. A Lumonics Inc. FQ class 1064 nm, 40 J neodymium–glass laser with $\approx$0.5 ms pulse length was used to heat a $\approx$1.6 mm diameter spot on the specimen, and the released deuterium was measured by a QMS ($m/e = 3$ and 4) located in the pumping line outside of the baking envelope. A single laser pulse, with heat loading of $\approx$1 J/mm^2, was sufficient to completely remove the film. The QMS was calibrated in situ using a known D_2 leak. The relative sensitivity to H_2 with respect to D_2 is known from previous calibrations with an H_2 leak [9], and the sensitivity to HD is taken to be the average of the H_2 and D_2 sensitivities.

3. Results and discussion

3.1. Chemical erosion of the divertor specimens due to D^+ impact

The oxygen content of the tiles, as measured by XPS, is believed to be largely due to air exposure after removal from DIII-D. We expect that this surface

coverage will be quickly removed from the surface during D^+ bombardment, and thus have no effect on the erosion measurements.

3.1.1. Upper divertor specimen UD4

Preliminary chemical erosion experiments were performed at 200 eV/D^+ and 300 K for fluences 3×10^{21} to $\sim 3 \times 10^{22}$ D^+/m^2. The erosion yield was found to be independent of fluence, and therefore, subsequent measurements were made at a fluence of $\sim 3 \times 10^{21}$ D^+/m^2. Fig. 3 shows the methane and total carbon ($\sum_i C_i D_j$) erosion yield for 50 and 200 eV/D^+ for temperatures of 300, 500, and 700 K. The erosion yield of pyrolytic graphite (PG) has also been plotted for comparison [7].

In the case of 200 eV/D^+ irradiation (Fig. 3(a)), at 300 K, the yields are 2–3 times higher than the corresponding yields for PG, possibly due to the amorphous nature of the film; such soft a-C:H films are found to have higher erosion yields when exposed to low energy hydrogen [8]. At 500 K the yields for the UD4 specimen and PG are similar. However, at 700 K, the yields of UD4 are lower by a factor of 2 compared to PG. Here the UD4 erosion yields are similar to those of boron-doped graphites [5,6], where we see the suppression of

Fig. 3. Methane and total chemical erosion yields of UD4 for: (a) 200 eV/D^+, and (b) 50 eV/D^+ impact at 300, 500, and 700 K. The chemical erosion yield of PG [7] has been added for comparison. The lines are drawn to guide the eye.

the high temperature reaction channel at higher temperatures and energies [10].

In the case of 50 eV/D^+ irradiation (Fig. 3(b)), again the UD4 yields are higher than the graphite yields at 300 K. Also, a significantly larger contribution from the heavier hydrocarbons is observed, as expected when the ion energy is reduced [7]. However, for the 500 and 700 K cases, the UD4 yields are similar to the PG yields. Again, this is consistent with boron-doped graphite [5,6] where for lower incident energies, there is little to no suppression of the chemical erosion yields at higher temperatures [10].

3.1.2. Lower divertor specimen B3

For the lower divertor specimen B3, with 50 eV/D^+ energy at temperatures of 300 and 500 K, we found that already at a very low fluence ($\sim 10^{21}$ D^+/m^2) the chemical erosion yield reaches a steady-state value comparable to that of PG. Visual examination of the specimen revealed that the film had been completely eroded through to the graphite substrate. Whatever B-containing film was on the surface, it was removed sufficiently quickly that the film erosion measurements could not be separated from the normal transients which occur when an ion beam is incident on a new spot on a specimen. In the region where this particular specimen was located in DIII-D, a mix of inner strike point, private-flux, and outer strike point (OSP) plasma exposures occurred. During double-null plasmas, B3 was actually at the OSP, and it is probable that at the time of removal of the tile from the tokamak, this tile was more likely to have experienced net erosion than net deposition [5]. This is consistent with our results which show the erosion yield to be essentially the same as that for graphite.

3.2. Thermo-oxidation of the divertor specimens

Fig. 4 shows the deuterium content of both the upper and lower divertor specimens (UD4 and B3) as a function of oxygen exposure time at 523 and 623 K. In all cases, the deuterium content falls by $\sim 40\%$ within the first hour of exposure. After this time, at 523 K, the D content is seen to level off, whereas at 623 K the D content continues to drop. It is likely that the initial drop in the deuterium content represents the erosion of the surface film, and the remaining D is what was implanted in the carbon substrate. The levelled off amount of 2–3 $\times 10^{21}$ D/m^2 seen for the 523 K case is approximately the amount of implanted D^+ found in graphite for high fluence implantations with ion energies of up to 1 keV [11]. At 523 K, the temperature is not high enough to oxidize the implanted graphite substrate to remove the implanted D – hence the levelling off of the D content curve. At 623 K, however, oxidation of implanted graphite may be occurring [12], leading to reduced
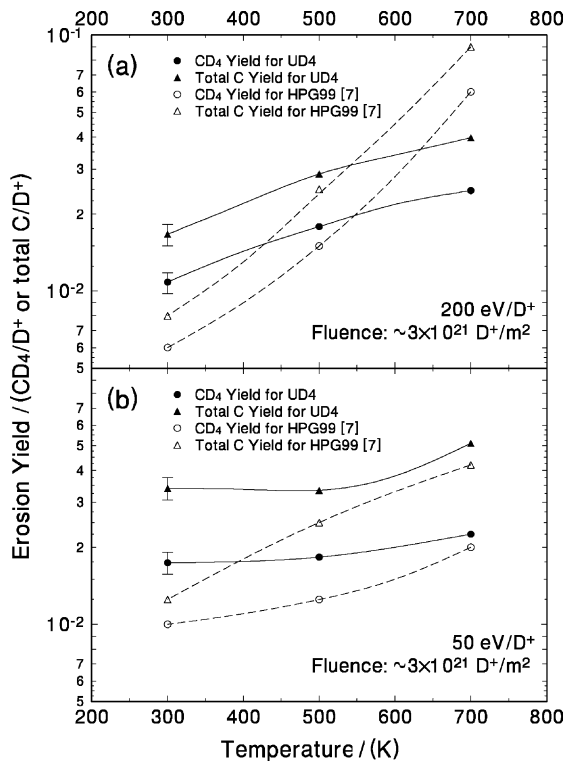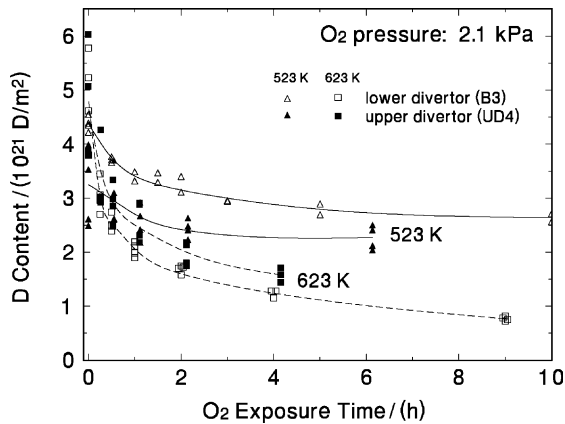
Fig. 4. Deuterium content of upper and lower divertor tile specimens as a function of O_2 exposure (at $\sim$2.1 kPa), as measured by laser desorption.

amounts of D remaining in the specimen with increasing O_2 exposure.

4. Conclusions

For the specimens removed from the DIII-D *upper divertor*, chemical erosion yields were found to be independent of fluence, up to $\sim$3 × 10^{22} D^+/m^2. Erosion yields were somewhat higher than the graphite yields at low temperature, however at higher temperatures, they were similar to boron-doped graphites. Surface analysis has confirmed the existence of large ($\sim$0.1 mm) crystals on the upper divertor specimens, and confirmed the existence of a small percentage of boron ($\sim$10 at.%) in the upper divertor films.

At the *lower divertor*, erosion measurements very quickly reached steady-state values comparable to that of pure graphite. The surface composition was primarily carbon with trace amounts of boron. The film thickness was estimated to be $\gtrsim 5$ nm. Visual inspection confirmed that even at a very low D^+ fluence ($\sim10^{21}$ D^+/m^2) the film had been eroded to the graphite substrate. It is likely that this tile was located in an area of net erosion just prior to its removal.

Deuterium content and thermo-oxidation measurements are consistent with the existence of very thin co-deposited layers on the divertor tiles. Much of the deuterium content is explained as being due to implantation of the tile substrate, as opposed to deuterium in a codeposited film.

The current erosion results do not provide any direct evidence as to why spectroscopic erosion yield measurements at the DIII-D lower divertor have shown a steady decline over an eight-year period of plasma exposures. They do, however, suggest that it is not a result of the boronizations.

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