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Chemical erosion of boronized films from DIII-D tiles

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Abstract

Tile specimens from the DIII-D tokamak have been studied to determine their erosion characteristics when exposed to D^+ ions and O_2 gas. Here, we report results for tile surfaces from the outer midplane. Surface analyses (EDX, XPS, SIMS) indicate that the surface layer is composed primarily of boron, with an overlayer of a B/C mixture. Total hydrocarbon ($\Sigma C_i D_j$) erosion yields were initially found to be $\sim$0.01–0.02 C/D^+, with limited variations due to D^+ energy (50 or 200 eV) or specimen temperature (300–700 K). Erosion yields were seen to decrease with fluence by a factor of 1.5–2 over the range $\sim 4 \times 10^{21}$–3×10^{22} D^+/m^2. Above $\sim 3 \times 10^{22}$ D^+/m^2 the yields level off. The initial erosion yields are found to be consistent with those for boron-doped graphite. O_2 gas exposure at 523 or 623 K initially removed $\sim$25% of the trapped D; however, the remaining D could not be removed by baking in O_2 at temperatures up to 623 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Boronization; Boronized carbon film; Chemical erosion; Co–deposition; DIII-D

1. Introduction

As described in [1], spectroscopic erosion data from the DIII-D tokamak have been compiled, and some striking historical trends have emerged. At the lower divertor, it was found that CD band emissions – an indicator of chemical erosion – have decreased by as much as two orders of magnitude near the inner strike point over the past 5–6 years. This reduction is thought to be related to the regular boronizations of the reactor vessel or some other plasma conditioning process [1]. It is important to note, however, that surfaces in the vicinity of the divertor strike points may be subjected to large net erosion or deposition rates. Thus, deposited boron may be quickly removed, or be covered by a thick deposit.

On the other hand, carbon influx measurements at the outer midplane [1] indicate erosion yields comparable to pure graphite. This is despite the fact that the ion flux to these surfaces is not considered sufficient to remove the deposited boron.

Both of these observations are somewhat counterintuitive, leading us to perform controlled laboratory measurements to aid in interpreting the tokamak results. The present investigation focuses on chemical erosion studies – both D^+ impact and thermo-oxidation in O_2 – of outer midplane specimens from DIII-D.

2. Experiment

2.1. Midplane tile specimens

The tile specimen is of UCAR-TS-1792 (ATJ) graphite, and was in the DIII-D outer midplane region through the 1993–1999 operational period. When viewed straight on, the tile has a distinct reddish coloring, and is somewhat speckled and non-uniform in appearance.

2.2. Surface analysis

A variety of surface analysis techniques were employed to provide information on the surface structure

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and composition. These are: (1) scanning electron microscopy (SEM), both of the surface and in cross-section; (2) energy dispersive X-ray spectroscopy (EDX), which gives compositional information over a depth of 2–3 μm; (3) X-ray photoelectron spectroscopy (XPS), which gives compositional and bonding information over a depth of about 10 nm; and (4) secondary ion mass spectrometry (SIMS), which has been used to provide compositional depth profiles with a resolution of a few monolayers.

2.3. Chemical erosion due to D^+ impact

Chemical erosion measurements were performed using our low-energy ion gun facility described in [2]. This is an ultra-high vacuum facility which is conditioned by baking at 500 K for >24 h prior to experimentation. Further wall conditioning (to remove carbon) is performed by exposure of the vessel surfaces to atomic deuterium, produced by contact dissociation of D_2 gas on a hot W filament. After conditioning, the typical base pressure in the test chamber is $\sim 10^{-7}$ Pa, dominated by D_2. During ion-beam operation, the test chamber pressure is $\sim 10^{-4}$ Pa D_2. Mass-selected D_2^+ ions, at energies of 50 and 200 eV/D^+ bombarded the target at normal incidence. The beam flux was $1\text{–}1.5 \times 10^{18}$ D^+/m^2 s over a circular spot of ~ 20 mm^2 area; each erosion case (temperature/energy combination) was performed on a new spot on the specimen. (In this paper we use D^+ to distinguish incident particles even though the deuterium atoms in the D_2^+ ions will be neutralized upon impact with the surface.) In order to minimize changes to the specimen due to heating, experiments at 700 K were the last to be performed. The effect of heating, affecting D content and possibly causing C/B concentration changes, will be the subject of a future study. 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). The QMS was calibrated in situ with known leaks of CD_4, C_2D_4 and C_3D_6. Relative sensitivities for C_2D_2, C_2D_6 and C_3D_8 were estimated from previous calibrations; see Ref. [2].

Wall contributions to the erosion signals, due to low-energy D^+ ions reflecting off the target surface and interacting with the vacuum system walls, were estimated – after performing the erosion experiments at 700 K, the highest temperature used in this study – in the following manner. The specimen was allowed to cool to near 300 K and the D^+ beam was turned on. The hydrocarbon signals display a prompt rise as soon as the beam is turned on; this is followed by a slow increase of the signals as the specimen saturates with D. The prompt rise is considered to be the wall contribution due to reflected ions, and the subsequent slowly increasing signal is attributed to chemical reactions on the specimen. As noted above, in this study we did not explore the effect of heating on subsequent erosion yields at lower temperature, and thus during the background determination experiments we did not wait for steady state to be reached at 300 K. The estimated wall contribution to the measured signals was typically less than 20%, and uncertainty in this correction constitutes a major component of the error bars shown in Fig. 3. The magnitude of the wall corrections obtained in the present experiments was very similar to those obtained for pyrolytic graphite; for further details on background corrections, refer to [2].

2.4. Thermo-oxidation of the DIII-D tile surface in O_2

These experiments follow the methodology described in [3]. A 1064 nm, 40 J neodymium-glass laser (Lumonics Inc. FQ class) with a ~ 0.5 ms pulse length, was used to heat a small test spot on the specimen, ~ 1.6 mm diameter. Prior to laser desorption, the vacuum chamber was evacuated to a pressure $<10^{-6}$ Pa, mainly D_2. During laser desorption, the released deuterium was measured by a QMS located outside the baking envelope in the pumping line. QMS signals at $m/e = 2\text{–}4$ were monitored. The laser heat loading, ~ 1 J/mm^2, was such that the boron/carbon film was completely removed by a single laser pulse. Subsequent laser shots on the same spot released much smaller amounts of D, presumably around the periphery of the beam spot. For all measurements reported here, two shots were taken at each spot. The D content of four spots on the film was measured after each O_2 exposure. The mass spectrometer was calibrated in situ by a calibrated leak of D_2. The quadrupole's sensitivity to H_2 (relative to D_2) is known from calibrations with a H_2 leak, and the sensitivity to HD is assumed to be the average of the H_2 and D_2 sensitivities.

O_2 exposure was accomplished by backfilling the test chamber to the desired pressure, about 2.1 kPa (as used in our previous measurements [3]). This pressure was maintained constant during the O_2 exposure experiments, and was measured by a capacitance manometer. The entire spherical exposure/desorption chamber was enclosed in a baking envelope and heated to the desired temperature (523 or 623 K) by external heaters prior to the admission of O_2. The temperature was measured by two copper–constantan thermocouples attached to flanges near the specimen holder.

3. Results and discussion

3.1. Surface analysis

SEM photographs of the surface show a globular-looking surface, similar to other plasma-deposited films.

In cross-section (see Fig. 1) the film is seen to be 1–2 μm thick, and is clearly visible in the photograph.

EDX spectra indicate that the surface layer (within the EDX analysis zone of ~2–3 μm) contains a few at.% C, N and O, with trace amounts of Al, Si, S, Ca, and Cu. The remainder, ~90 at.%, is interpreted as being B. This implies a layer consisting mainly of B, extending to a depth of >2–3 μm. The amount of carbon measured in the film is consistent with the amount of C deposited with the boron during boronizations, 5–10 at.% [4].

The composition of the surface as determined by XPS is given in Table 1 for the initial surface, as received from DIII-D, prior to D^+ or O_2 exposure. Analysis was performed on the front surface and at two depths following sputtering. It was not possible to measure the sputtering beam current, and thus we have only a rough estimate of the sputtering depth (based on previous measurements of the sputter Ar^+ beam current): ~10 nm after the first and ~75 nm after the second sputtering.

For all three XPS measurement cases, boron bonding was primarily B–B. Before sputtering, there was some evidence for B–C and B–OD bonding, whereas at the sputtered depths, there was an increasing B–O component while the B–C and B–OD components disappeared. Carbon was found primarily in C–C bonds, however, the type of bond appears to change after sputtering. A small amount of C is also attributed to hydrocarbons. Surface oxygen is mainly in oxygenated hydrocarbons, while after sputtering an increase in the B–O component is observed.

A SIMS depth profile of the film is shown in Fig. 2; we note that the SIMS yields are not calibrated, and therefore the profiles do not represent relative concentrations. The sputtering rate is estimated to be ≈0.03 nm/s, based on the deuterium profile in a D^+-implanted pure carbon reference (HPG99 pyrolytic graphite from Union Carbide). There is clearly a carbon component in the film, extending to a depth >30 nm, however, the surface peak observed by XPS is not seen. Boron, oxygen and deuterium are also seen in the SIMS profiles, but it is noted that over the first 10 nm there appears to be an increase in both B and D with depth. In the case of B, this is consistent with the XPS results, where the B concentration was observed to increase from 34 to 56 at.% in the first ~10 nm. Changes in sputter sensitivity, due to variations in the matrix in the first 10 nm of the film, are thought to be responsible for the strong increase in all SIMS signals right at the surface, and for possibly obscuring a decrease in the C concentration with depth. Between 30 (~1 nm) and 300 s (~10 nm) of

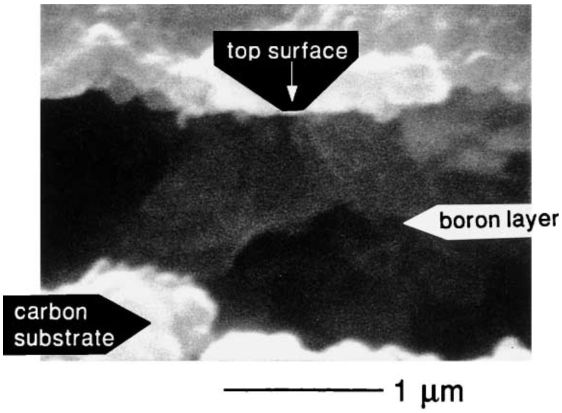

Fig. 1. Cross-sectional SEM photo of the midplane tile surface. The boron layer appears darker than the carbon substrate and the epoxy casing because the boron layer was harder than the other two materials, and the specimen could not be polished evenly.

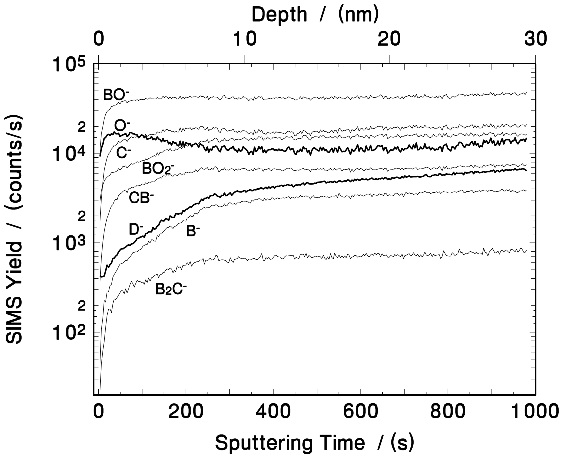

Fig. 2. SIMS depth profile, obtained in the negative ion mode. Sensitivity calibration for the various elements was not performed.

Table 1
Surface composition of DIII-D outer midplane tile specimens prior to D^+ or O_2 exposure, as measured by XPS. The composition does not include H or D components

	B	C	O	N	B/C
Front surface	34 at.%	43 at.%	19 at.%	3–4 at.%	0.8
~10 nm depth	56	23	17	3–4	2.4
~75 nm depth	63	19	15	3–4	3.3

sputtering, the B^-/C^- ratio increases by a factor of 4, consistent with the changes observed in the B/C ratio by XPS where the corresponding ratio change is a factor of ~3 (i.e., B/C ~0.8 at the surface and 2.4 at ~10 nm depth; see Table 1).

The various surface analyses of the tile lead us to conclude that there is a thick layer of plasma-deposited B (introduced during boronization) covering the graphite tile. On top of the boron is a thin layer, possibly as thick as 100 nm, containing a significant amount of C (~20 at.%). The overall thickness of the boron layer (~2 µm) is consistent with the amount of B introduced into DIII-D during boronizations (~3–5 µm averaged over the entire surface area [1,5]). The surface carbon layer implies that there is a net deposition of carbon from the plasma onto the midplane surfaces.

3.2. Chemical erosion due to D^+ impact

Chemical erosion yields have been measured for 50 and 200 eV/D^+ impact and specimen temperatures of 300, 500 and 700 K. Erosion yields are shown as a function of fluence in Fig. 3. The fluence dependence of the methane and total (i.e., $\Sigma C_i D_j$) chemical erosion yields are generally similar, with the total C yields about twice the methane yields. For comparison with pyrolytic graphite, selected curves are reproduced here from Ref. [2]; see Fig. 4. At room temperature, the initial total chemical erosion yields (~0.01–0.015 C/D^+) from the DIII-D tile are essentially the same as those for pyrolytic graphite [2]; however, the total yields for the DIII-D tile decrease by about a factor of 2 with increasing fluence over the range ~4×10^{21}–3×10^{22} D^+/m^2. At 500 K, the initial total yields are only marginally higher than the 300 K yields, and thus are about a factor of 2 lower than yields from graphite under the same conditions [2]. (We note that the 50 eV experiments at 500 K were the first to be performed, and there was some uncertainty about the fluence measurement due to changes in the beam operating conditions, possibly causing the apparent shift of the curve.) At 700 K and 50 eV, the initial total yields are again about 0.01–0.015 C/D^+, however, the total yields for 200 eV D^+ are initially above 0.02. In both 700 K cases, the initial yields are ~4 times lower than those for graphite. Again, the yields decrease a further factor of 1.5–2 with increasing fluence (see Fig. 3).

The initial erosion yields are consistent with yields from boron-doped graphites which have substantially lower yields than pure graphite at temperatures above 600 K and energies above ~100 eV, but similar yields at low energy and low temperature [6,7]. The decrease in

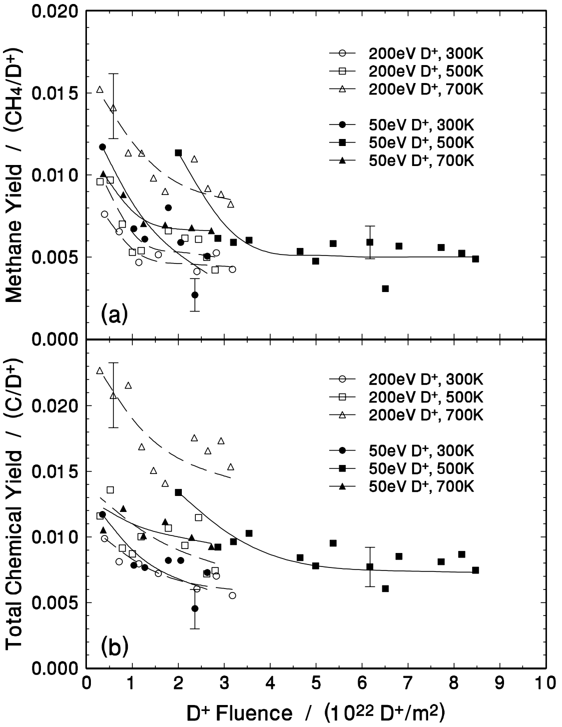

Fig. 3. Fluence dependence of D^+ erosion measurements: (a) methane yields and (b) total chemical erosion yields based on the sum of the erosion yields for the hydrocarbons: CD_4, C_2D_2, C_2D_4, C_2D_6, C_3D_6 and C_3D_8.

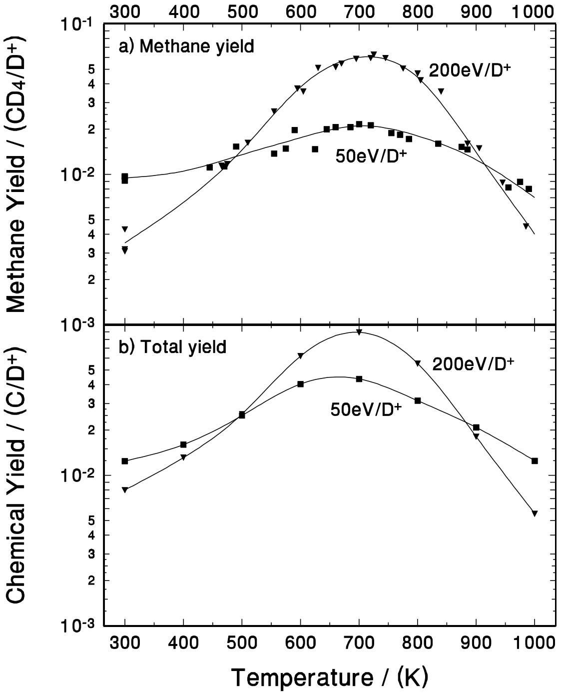

Fig. 4. Methane (a) and total chemical erosion (b) yields as function of specimen temperature for D^+ impact on pyrolytic graphite; from Ref. [2].

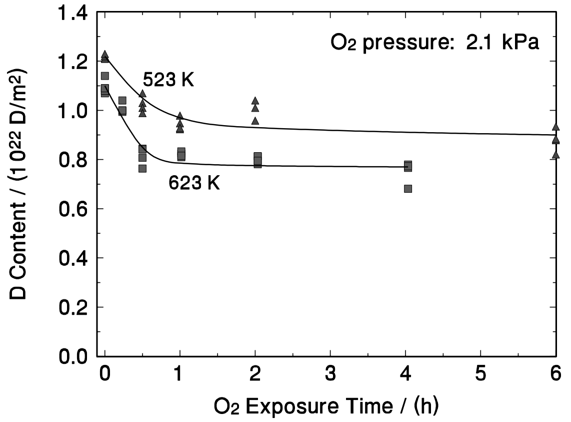

Fig. 5. D content of the midplane tile as a function of O_2 exposure, as measured by laser desorption.

yield with fluence is consistent with the preferential removal of carbon from the surface layer, leading to a boron enriched film [8,9]. The fact that the yields do not decrease to zero may indicate that the yields are limited by the removal of boron, or by the diffusion of carbon atoms through the boron-rich layer to the surface. The fact that the 700 K steady-state levels are higher than the 500 K levels, which are in turn higher than the 300 K levels, may indicate that carbon diffusion is an important factor.

3.3. Thermo-oxidation of the DIII-D tile surface in O_2

The deuterium content of the films, as a function of O_2 exposure time, is shown in Fig. 5. At both 523 and 623 K, the D content falls by about 25% after an hour or less of O_2 exposure at 2.1 kPa, but thereafter remains fairly stable. This result is consistent with the removal of the surface carbon layer (and the D trapped within it), leaving a stable boron-rich surface behind. The remaining D may have been trapped during the boron deposition process (during boronization), or may have been co–deposited with carbon, during tokamak discharges, and later buried beneath a boron deposition. Similar thermo-oxidation experiments on other tokamak codeposits [10] have generally led to the removal of the entire codeposit. Thus, the boronization process has the effect of locking up trapped deuterium.

4. Conclusions

All of the surface diagnostics performed give a more-or-less consistent picture of the midplane tile surface. The surface material consists of a B-rich layer of ~2 μm thickness – formed during boronization – on top of which sits a thin layer of co–deposited C/B/D, with 20–40 at.% C.

D^+ chemical erosion experiments at 300 and 500 K give initial erosion yields of 0.01–0.015 C/D^+, which are similar to both pure graphite and B-doped graphite yields under the same conditions. At 700 K, the initial erosion yields are four times lower than the pure graphite case, which is consistent with the erosion of B-doped graphites. The erosion yields were found to decrease with fluence over the range $\sim 4 \times 10^{21}$–3×10^{22} D^+/m^2, and this is interpreted as being due to the depletion of carbon from the 'thin' surface layer.

In DIII-D, the midplane tile surfaces receive D^+ fluxes of $\sim 4 \times 10^{20}$ D/m^2 s [4], with shot durations of ~5 s; hence, a total fluence of $\sim 2 \times 10^{21}$ D/m^2. This would not be sufficient to remove the surface carbon layer, and consequently erosion yields at the tokamak midplane could appear to be similar to graphite for the duration of a discharge.

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