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Oxygen removal of codeposited a-C:D layers from tokamak tiles

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Abstract

To investigate the thermo-oxidative removal of hydrogen from codeposited layers formed in tokamaks, codeposited specimens from a TFTR bumper limiter tile and from JET and DIII-D divertor tiles have been exposed to O_2 gas at 523 and 623 K. From D-content measurements, derived erosion rates were found to be several micrometers per hour, with faster erosion rates obtained for thicker codeposits. Erosion rates at 523 K could be increased by increasing the O_2 pressure above the nominal pressure of 2.1 kPa; at 21 kPa, the initial erosion rate was ~5 times as fast. To study the effect of water on the film erosion and D removal rates, specimens were exposed to pure water vapour. Although water vapour alone was found to decrease the D-content of the films after 'short' exposures, 'long-term' exposures to H_2O had no additional effect, consistent with an isotope exchange mechanism. Exposure to air led to similar erosion rates as observed with O_2, for an equivalent O_2 partial pressure, indicating that the other constituents in air had no significant effect on the chemistry. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the largest operational and safety concerns in the design of next generation tritium-burning fusion reactors is the accumulation of tritium in codeposited films. Such layers are formed through the redeposition of eroded carbon atoms in conjunction with a large flux of D/T fuel particles. On surfaces where the carbon erosion rate is less than the incident flux of carbon, it is feared that such layers may grow, reaching thicknesses of hundreds of μm. In cases where the surface temperatures are lower than that required for the detrapping and release of the hydrogen, large amounts of hydrogen may be trapped, leading to significant tritium inventory.

Because the growth of such films is often greatest on surfaces which are somewhat hidden or sheltered from the main plasma, such as in between tiles, it is necessary to develop a removal technique which will not be restricted from accessing these areas. This must be true, even in the presence of a very strong magnetic field. While oxygen is not a favoured gas as far as tokamak operation is concerned, it is the basis for most techniques suggested for codeposited film removal [1]. By far, the easiest approach is to use O_2 gas without the benefit of atomization or ionization. It must be demonstrated, however, that thick codeposited layers may be removed at reasonable rates, at temperatures accessible to the various reactor components. A review of other codeposited film removal techniques is given in Ref. [1].

There have been some encouraging results, indicating that O_2 may indeed provide adequate erosion rates, coupled with hydrogen removal. In the context of radiation release during accidental air exposure, Causey et al. [2] found that essentially all of the deuterium was removed from a codeposited layer (~50 μm thick) from TFTR by heating in air for 1 h at 623 K, implying film erosion rates >50 μm/h. In earlier experiments [3], we have also found erosion rates in excess of 10 μm/h for a thick codeposit from TFTR. Experiments with laboratory-produced films showed that oxygen exposure leads

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to C erosion via CO and CO_2 formation, and D removal via D_2O formation; no CD_4 and only small amounts of D_2 were detected [4]. Wang et al. [5] have also reported that O_2 exposure has led to the removal of both deuterium and carbon from codeposited layers produced in ASDEX-Upgrade. At 650 K, they measured C erosion rates of ~0.3 μm/h; however, the films were deposited on a Si substrate, and were much thinner (0.75 μm), factors which could affect the film structure. The inclusion of some boron in the film [5] may also have affected the erosion.

Several questions remain as to the suitability of the thermo-oxidative technique in a reactor environment. Firstly, it is necessary to investigate the behaviour of codeposits (including those with impurities) from several fusion devices. Also, a greater understanding as to why the erosion rates are orders of magnitude larger for tokamak films, in comparison with graphite and some laboratory-deposited films, is desired.

The purpose of the present study is to measure the erosion of codeposited layers from different tokamaks due to O_2 exposure, to look at the effect of different atmospheric gases on the erosion, and to see what might be done in order to increase our understanding of the mechanism.

2. Experiment

2.1. TFTR tile specimens

During the November 1985 to July 1987 operation period, the inner bumper limiter of TFTR was protected by tiles of POCO AXF-5Q graphite mounted on water-cooled Inconel backing plates [6]. These tiles were exposed to a large number of deuterium discharges, resulting in regions of extensive erosion and redeposition [7]. During the 1987 opening, in situ analyses of metal impurities were made [6], and 33 of the 1920 tiles were removed for further analysis [2,6–10]. In our previous study [3], the specimens were cut from the surface of a tile which was in the region of moderate deposition; the tile is referred to as N3-15 in other publications [7,10]. In the present study, the specimens are cut from a tile designated N3-24, which was located at the top of the limiter column. D content measurements by Wampler et al. [7] indicate $\sim 7 \times 10^{21}$ D/m^2, placing it in a region of low deposition. Metallic concentrations were measured to be $\sim 2 \times 10^{21}$ atoms/m^2 [6,7].

In our previous publication [3], we based our film thickness (for tile N3-15) on cross-sectional photographs from Ref. [6]. We have since had our own cross-sectional SEM photographs made, revealing significantly different results. Instead of ~30 μm as shown in Ref. [6], the film on our N3-15 specimens was ~5 μm thick; see Fig. 1(a). This means that density values must be increased by a factor of 6, to ~1900 kg/m^3 from the 320 kg/m^3 estimate used in Ref. [3]. Film removal rates are proportionately decreased. At present, we have no explanation for the noted differences in the cross-sectional photographs, other than possible variations at different locations on the tile.

For the current specimen, (N3-24), the codeposited layer is too thin to be seen in cross-sectional SEM photographs; see Fig. 1(b). For approximate erosion measurements of tile N3-24, the measured D/C ratio for tile N3-15 (~0.35) Ref. [3], and a density of 1900 kg/m^3 are used. This gives an initial film base thickness of 0.1–0.2 μm for the N3-24 specimens.

2.2. JET divertor tile specimens

The JET carbon tile used in the current experiments is from the JET Mark I divertor, in operation from April 1994 to March 1995. The tiles were made from a 2D carbon fibre reinforced graphite with the weave plane normal to the plasma-facing surface. The tiles were mounted on a water-cooled support bar. A description of the tile placements, their operational history, and surface analysis information is found in Ref. [11]. Our tile was located in position 6A. In an ion-beam analysis scan over the tile, the shadowed region was found to have up to 3×10^{23} D/m^2, while plasma-exposed regions had lower D content. A significant Be content was also observed: of the order of 10% in unshadowed regions, but less in shadowed regions. Cross-sectional SEM photographs indicate a film thickness of 2 ± 0.5 μm; see Fig. 1(c).

2.3. DIII-D divertor tile specimens

The DIII-D tile was of UCAR-TS-1792 graphite, and was installed in DIII-D from March 1989 to December 1989. It came from the lower divertor and is the second tile from the inboard wall, along the 105° line. The designation 6410#B is used to describe the tile. The tile was exposed to ~1500 lower divertor discharges with D_2 working gas during nine months of operation. Further information about the tile is given in Ref. [12]. During the tile's operational period in the tokamak, about 40% of the interior of the machine was covered with graphite tiles, the remainder was Inconel. X-PIXE scans for metals on the 'plasma-facing surface' indicate concentrations of $\sim 5 \times 10^{21}$ atoms/m^2 [12]. D concentrations vary from $\sim 6 \times 10^{22}$ D/m^2 towards the inboard wall to $\sim 2 \times 10^{22}$ D/m^2 toward the inboard edge of the tile [12]. Specimens were cut from both the 'plasma-facing surface' (from the outboard edge) and the 'side' (from the inboard edge) of the tile. An interesting aspect of the codeposited layer on this tile is that it was very likely formed under detached divertor conditions, with $T_e < 2$ eV [13].

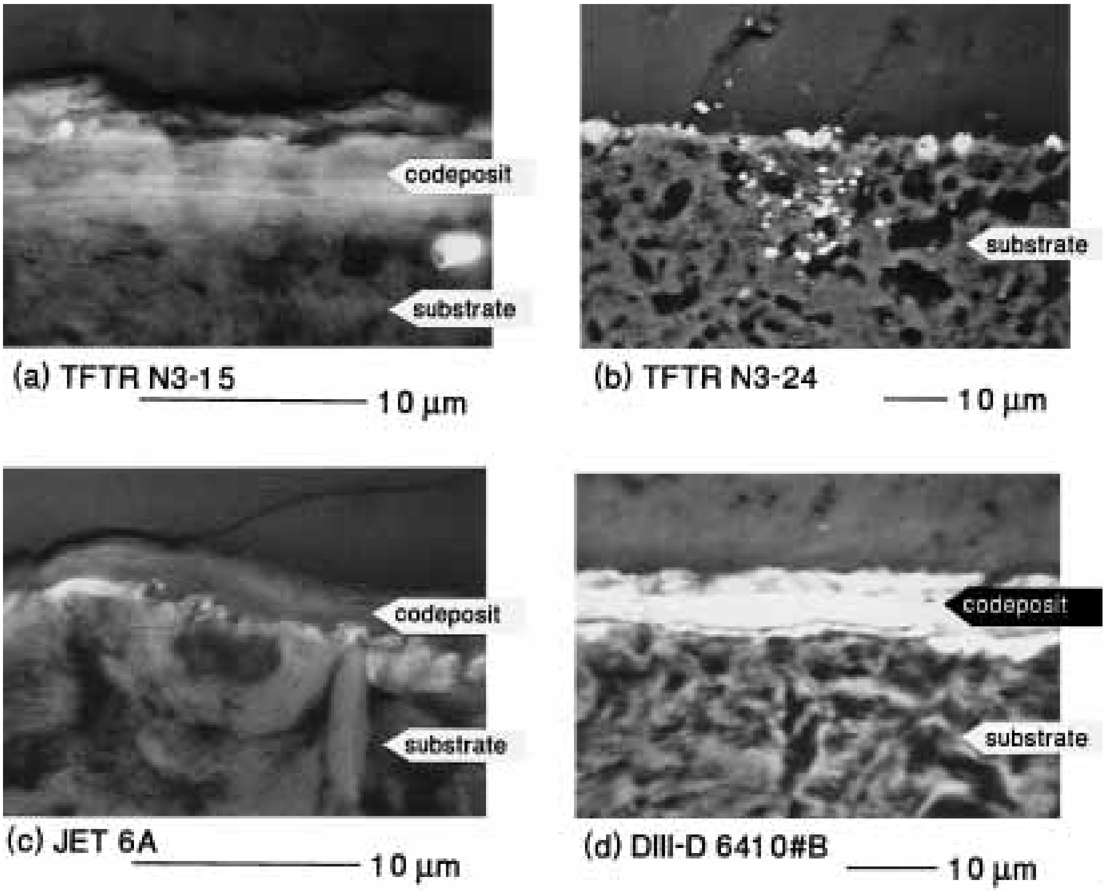

Fig. 1. Cross-sectional SEM photographs of the tokamak tiles studied. (a) TFTR N3-15 (erosion results presented previously in [3]), (b) TFTR N3-24, (c) JET 6A, and (d) DIII-D 6410#B. All photographs shown have been taken in the backscattering/compositional mode, in which heavier elements show up as a brighter image. For the TFTR N3-15 and DIII-D specimens (parts a and d), the codeposited layers appear brighter than the carbon substrate due to a significant Ni concentration. For the JET specimen (part c), the main metallic impurity is Be, which does not give contrast against carbon. In this case, the codeposited layer is observable due to structural differences with the C/C composite substrate. For the TFTR N3-24 specimen (part b), the codeposited layer is too thin to be seen in the photograph.

Cross-sectional SEM photographs of the DIII-D codeposited layer from the 'plasma-facing surface' reveal a film thickness varying from <1 to >5 µm. An average value of ~2 µm has been assumed for the erosion rate calculations. Variations in film thickness were observable, without magnification, as streaks along the surface. A photograph of the thick region of the film is shown in Fig. 1(d).

2.4. D content measurements

As part of the present study, the D content of the codeposited layers was measured by laser thermal desorption spectroscopy (TDS). The film specimen was mounted on a holder in a spherical test chamber; see Fig. 1 in Ref. [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 TDS the vacuum chamber was evacuated, with background pressures being $<10^{-6}$ Pa. During TDS, the released deuterium was measured by a quadrupole mass spectrometer (QMS) located outside the baking envelope in the pumping line. QMS signals at $m/e = 3$ and 4 were monitored. In test runs monitoring $m/e = 5$ and 6, or 18 and 20, it was found that no significant amounts of tritium (<0.1% of the $m/e = 3$ plus 4 signals) or water (<0.5% of the $m/e = 3$ plus 4 signals) were released. The laser heat loading, ~1 J/mm^2, was such that the 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 one or more spots on the film was measured after each O_2, H_2O or air exposure; see below. The mass spectrometer was calibrated in situ by a calibrated leak of D_2. The quadrupole's relative sensitivity to H_2 (relative to D_2) is known from calibrations with an H_2 leak, and the sensitivity to HD is assumed to be the average of the H_2 and D_2 sensitivities.

2.5. O_2, H_2O and air exposure

Gas exposure was accomplished by backfilling the spherical test chamber to the desired pressure, generally about 2.1 kPa. This pressure was maintained constant during the gas exposure experiments, and was measured by a capacitance manometer. The entire spherical exposure/desorption chamber (enclosed in a baking envelope) was heated to the desired temperature by external heaters prior to the admission of gases. The temperature was measured by two copper-constantan thermocouples attached to flanges near the specimen holder, and by a mercury thermometer located within the baking envelope, just outside the spherical chamber, near the two flanges with thermocouples. The amount of reactive gas (O_2 or H_2O) in the sphere was ~2 orders of magnitude larger than the carbon content of the film specimens, ensuring that the gas supply was not limiting the C removal rate. The pumping time constant of the sphere during gas exposure was ~1–10 h. A mass spectrum taken during O_2 (H_2O) exposure confirmed that O_2 (H_2O) was the primary species flowing out of the sphere.

Exposures were made with O_2 (99.9% purity), water vapour and humid air. Water vapour was introduced into the system from a sealed reservoir containing distilled water at room temperature. The water was outgassed under vacuum for about 1/2 hour in order to remove dissolved gases. The room-temperature vapour pressure of water, ~2.8 kPa, was sufficient to backfill the test chamber to the desired 2.1 kPa. Exposure to humid air was accomplished by drawing air, at atmospheric pressure, from a 25 *l* reservoir containing several litres of water. With the water at room temperature, the approximate composition of the air admitted to the test chamber was: 10 kPa total: 2.1 kPa O_2, 0.28 kPa H_2O, 7.6 kPa N_2.

2.6. Mass loss experiments

Mass loss measurements were carried out by weighing film specimens (not used for laser desorption) before and after exposure to O_2. Specimens were weighed under atmospheric conditions using an electronic balance (Ohaus AP 250D), with a sensitivity of 10 μg. Measurements were only made on the DIII-D specimens, as the TFTR N3-24 codeposit was too thin, and the JET codeposit too non-uniform. In addition to the codeposited specimens, pieces of the substrate material from all three tiles were also tested. After 4 h of O_2 exposure at 623 K and 2.1 kPa, no measurable change in mass was observed for any of the substrate specimens, confirming that graphite is stable against O_2 at this temperature. This is consistent with our previous findings [3].

3. Results

3.1. TFTR specimens

The erosion of TFTR codeposited specimens (tile N3-24) is shown in Fig. 2(a) for exposure to O_2 at 523 and 623 K, and air at 523 K. Erosion due to exposure to H_2O is shown in Fig. 2(b). As with our experiments with thicker TFTR N3-15 codeposits [3], the majority of the film was removed in <1 h at 623 K, and in ~10 h at 523 K. In the present case (tile N3-24), however, the initial D concentration (and presumably the film thickness) was found to be a factor of 30 smaller. The effects of humid air and O_2 were quite similar at 523 K, which was expected, as the O_2 partial pressures were the same. The

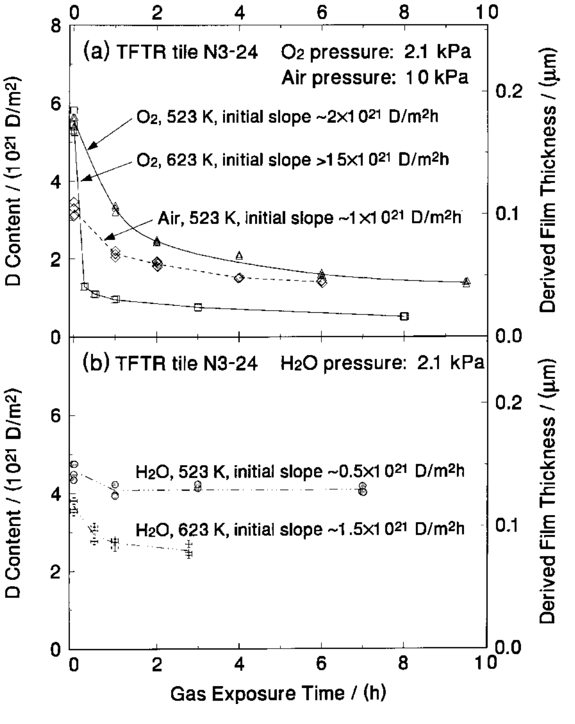

Fig. 2. D content of the TFTR codeposited film (tile N3-24), as measured by laser desorption. (a) as a function of O_2 or air exposure time, and (b) as a function of H_2O exposure time. Thicknesses were derived from the D-content measurements, by assuming the density and D/C ratio found for the N3-15 tile.

initial D content of the tile was measured to be 3–6 × 10^{21} D/m^2, in good agreement with the measurement of ~7 × 10^{21} D/m^2 of Wampler et al. [7]. We found variations in D content to be less than a factor of 2 for locations 30–40 mm apart.

Exposure of the films to water vapour led to different erosion profiles, see Fig. 2(b). The measured D content initially decreases with time, and then reaches a plateau for both temperatures. We attribute the noted initial decrease in D content to isotope exchange. This result is very similar to that observed by Chiu and Haasz [14], where the chemical removal of D from ion-implanted graphite was studied. For H_2O exposure at 570 K, they saw an initial release of 10–20% of the D content, followed by steady levels [14]. It is concluded that water vapour on its own is not very effective for codeposited film removal at these temperatures. The above results on the exposure of the films to humid air, Fig. 2(a), also indicate that water does not have a large effect when in combination with O_2.

3.2. JET specimens

Like the TFTR specimens, the JET codeposited films were exposed to O_2 gas at 2.1 kPa and temperatures of 523 and 623 K. The specimens of tile used for these measurements were from the region of thickest codeposit as indicated in Ref. [11]. Results of the experiments are shown in Fig. 3. The initial D content measured, 3–4 × 10^{22} D/m^2, is a factor of 3 lower than that given by Coad et al. [11]; the reason for this discrepancy is not known. However, we found that the D content varied strongly over the tile, on the mm scale; this is consistent with the findings in [11]. On exposure to O_2, the D concentration was reduced in a similar manner to other codeposits studied. In particular, most of the D from the film was removed in less than 1 h at 623 K. By assuming that the density and D/C ratio were uniform through the film, erosion rates in μm/h could be derived, although, the density and D/C ratio could not be determined without a measure of the carbon content.

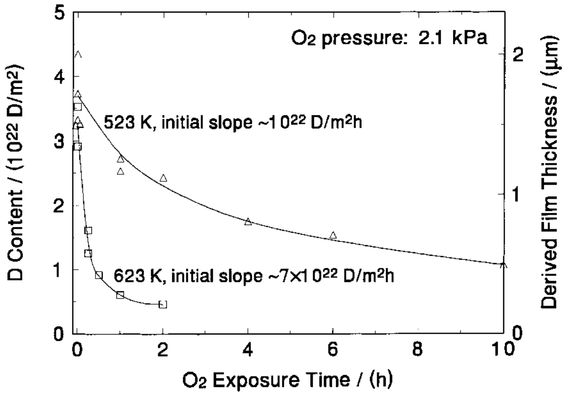

Fig. 3. D content of the JET codeposited film as a function of O_2 exposure time, as measured by laser desorption. Thicknesses were derived from the D-content measurements, by using the initial thickness as determined from the SEM cross-sectional photographs, and assuming a constant D/C ratio.

3.3. DIII-D specimens

The removal of deuterium from a specimen cut from the 'plasma-facing surface' of the DIII-D tile during O_2 exposure is illustrated in Fig. 4. The initial D concentration of ~2 × 10^{22} D/m^2 agrees well with the measurements of Walsh et al. [12] on the outboard side of the tile. In comparison with the TFTR and JET film erosion rates, the DIII-D codeposited layer appears to be removed more slowly by O_2, particularly at 523 K. Also, in contrast to the TFTR and JET specimens studied, the removal of the film was clearly visible. It is thought that the apparent slower removal is related to the non-uniformity of the codeposit, as observed visually, and noted on the SEM photographs. Mass-loss measurements made at 623 K allow us to determine the

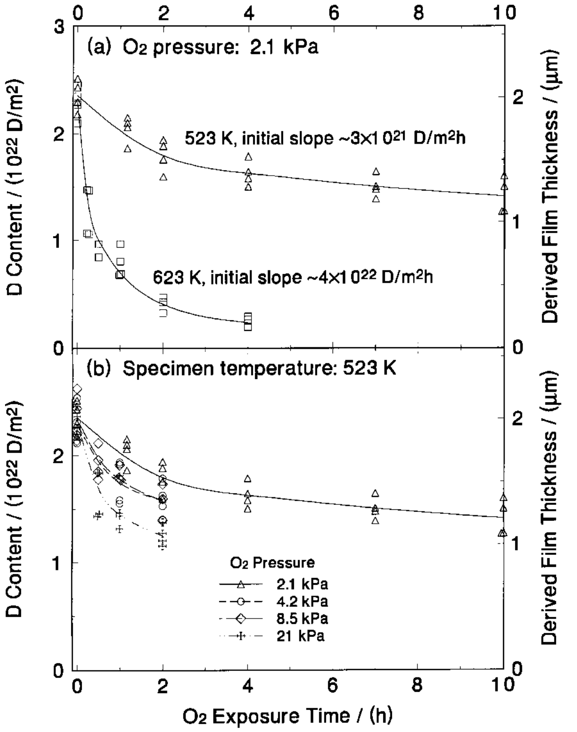

Fig. 4. D content of the DIII-D codeposited film as a function of O_2 exposure, as measured by laser desorption. (a) Erosion at different temperatures, and (b) erosion at different O_2 pressures. Thicknesses were derived from the D-content measurements, by using the initial thickness as determined from the SEM cross-sectional photographs, and assuming a constant D/C ratio.

D/C ratio for the film. On a piece of tile, with surface area $\sim$123 mm^2, a 280 µg mass loss was measured after 4 h of O_2 exposure. This corresponds to 1.1×10^{23} C/m^2, giving a D/C ratio of 0.18. For a nominal film thickness of 2 µm (as estimated from the SEM photographs), this implies a density of 1300 kg/m^3.

In Fig. 4(b), we show the results of experiments investigating the effect of O_2 pressure on the film removal rate. Tile specimens were exposed to O_2 at 523 K at pressures in the range 2.1–21 kPa. It was found that the initial erosion rate (derived from D-content measurements) could be increased by a factor of 5 by increasing the O_2 pressure from 2.1 to 21 kPa. It is not known whether such an increase would also occur at higher temperatures.

Film removal measurements were also made for codeposited layers on a specimen cut from the 'side surface' of the DIII-D tile. Near the top (i.e., close to the plasma-facing surface) of this specimen, the D content was $\sim 10^{21}$ D/m^2, while from $\sim$3 mm below the top edge to the bottom ($\sim$25 mm below the top), the D content was $\sim 7 \times 10^{20}$ D/m^2. O_2 erosion measurements at 523 and 623 K showed similar behaviour to film removal on the 'plasma-facing surface' discussed above.

4. Summary

A comparison of D-removal and film erosion rates for various tokamak codeposits is provided in Table 1. Generally, it is seen that the thicker the codeposit, the faster the removal rate. Removal rates of a few µm/h or more have been found for all tiles studied in our experiments. In contrast, the removal rate for an ASDEX-U codeposit was reported to be an order of magnitude slower [5], possibly due to a different structure (being deposited on Si), or the presence of B impurities. In all of our result, the D-removal rates tend to decrease as the films get thinner. It is thought that this is due to a change in film structure close to the graphite substrate. Erosion rates at 523 K could be increased by increasing the O_2 gas pressure above our nominal value of 2.1 kPa; at 21 kPa, the initial erosion rate was $\sim$5 times as fast. Reactions with water vapour were not found to be effective – relative to oxygen – at removing the D from the codeposited layers at the temperatures studied, while the D-removal rate due to humid air exposure was similar to that obtained for pure oxygen at an equivalent O_2 partial pressure. All of the tiles studied here had significant amounts of metal contamination, indicating that metals do not restrict the oxidation process. It is even possible that the metals act as a catalyst, thus explaining the high erosion rates observed for the films, as compared to the graphite substrates.

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Table 1
Erosion and D removal rates from codeposited layers on (a) TFTR bumper limiter tiles and (b) tokamak divertor tiles

(a)	Temp. (K)	TFTR tile edge [2] ($\sim$50 µm) 101 kPa air	TFTR N3-15 [3] [a] ($\sim$50 µm) 2.1 kPa O_2		TFTR N3–24 ($\sim$0.15 µm) 2.1 kPa O_2	
		derived erosion rate (µm/h)	derived erosion rate (µm/h)	D removal rate (10^{21} D/m^{2}h)	derived erosion rate (µm/h)	D removal rate (10^{21} D/m^{2}h)
	523		0.8	20	0.07	2
	573		3.5	100		
	623	>50	>10	>250	>0.5	15

[a] Based on an initial film thickness of $\sim$5 µm and a density of $\sim$1900 kg/m^3.

(b)	Temp. (K)	ASDEX-U [5] (0.75 µm) 101 kPa air	JET divertor 6A ($\sim$2 µm) 2.1 kPa O_2		DIII-D 6410#B ($\sim$2 µm) 2.1 kPa O_2	
		measured erosion rate (µm/h)	derived erosion rate (µm/h)	D removal rate (10^{21} D/m^{2}h)	derived erosion rate (µm/h)	D removal rate (10^{21} D/m^{2}h)
	523		0.5	10	0.23	2.7
	623	0.3 (650 K)	3.3	70	3.5	41

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