



# The removal of codeposited layers from TFTR tiles by O<sub>2</sub> gas exposure

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## Abstract

Graphite tiles from the TFTR inner bumper limiter have been exposed to O<sub>2</sub> gas at 2100 Pa and 523–623 K in order to remove codeposited carbon/deuterium layers. It was found that most of the codeposited layer was removed at a rate ~3 orders of magnitude faster than that observed for thinner laboratory plasma deposited films. Such fast erosion may make removal of codeposited films in ITER by O<sub>2</sub> gas exposure a reasonable option. © 1998 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 ITER is the accumulation of tritium in codeposited films. These layers are formed from the tritium fuel and eroded carbon atoms (or hydrocarbon molecules/radicals) on surfaces where carbon erosion rates are less than the incident carbon flux, resulting in the net deposition of material. Often, the heat loading on such surfaces is such that the surface temperatures are below that required for the desorption of hydrogen from the codeposited layers. Various techniques have been proposed for the removal of these layers, many of which involve the use of oxygen. The easiest approach is to expose the surfaces to molecular oxygen at elevated temperatures. At 623 K, the erosion of graphite in air or oxygen is negligible [1], but codeposited films have a different structure, and thus may behave quite differently. In earlier experiments, presented here for comparison, we have exposed a thin (2 µm) laboratory plasma-deposited film to O<sub>2</sub> gas at 2100 Pa and 623 K, and found erosion rates <10 nm/h. Such erosion rates could be projected to 1000s hours exposure to O<sub>2</sub> for films 100s µm thick. Clearly, this cannot be an acceptable operating scenario for ITER.

There is, however, evidence that the thick deposits observed in tokamaks may be removed more quickly than the thin plasma-deposited films produced in the laboratory. Causey et al. [2] found that the tritium content of a TFTR codeposited layer on the side of a tile (surfaces perpendicular to the plasma-facing surface) was almost completely removed after 1 h at 623 K in air. He observed, however, that the film itself appeared to be unaltered [3], so it is uncertain whether the carbon content of the film was also removed. More recently, Wang et al. [4] have reported that O<sub>2</sub> 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, their calculated film density is about 5 times higher than the estimated 'effective' density for our TFTR tile.

The purpose of the present experiments is to further explore the T-removal and film erosion behaviour of codeposited layers formed in tokamaks. Here we present results for codeposited layers formed in TFTR during D–D operation during the 1980s [5,6].

## 2. Experiment

### 2.1. Laboratory film specimen

The film specimen was prepared for us by DIARC-Technology Inc., Helsinki, Finland, and consists of a

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D-containing carbon film ( $\sim 2 \mu\text{m}$  thick) plasma deposited on a stainless steel substrate (with diamond-like carbon and W interlayers). The film was deposited from a 60 eV  $\text{C}^+$  plasma, produced by an arc discharge, with a  $\text{D}_2$  background gas. The substrate temperature was kept below 373 K during the deposition process. The density of the film, as measured by Rutherford backscattering analysis, is  $2600 \text{ kg/m}^3$  [7], and the test specimen had a film surface of  $13.5 \times 15 \text{ mm}^2$ .

## 2.2. TFTR tile specimen

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 [5]. During the 1987 opening, in situ analyses of metal impurities were made [6], and 33 of the 1920 tiles were removed for further analysis [2,5,6,8–10]. The specimens used in the present study 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 [5,10]. Metal contamination on the tile was measured by electron microprobe analysis to be  $<0.2 \text{ at.}\%$  in Ref. [10]; however, somewhat higher concentrations of equivalent Ni deposition (1–2 at.%) were found in [5,6]. Electron micrographs of the front surface and cross-sections of the front surface, as well as SIMS depth profiling of this tile are available (figs. 4(c), 5 and 7 in [6]). A complex surface structure is well developed, which leads to a large increase in effective surface area. The cross-sectional photos (fig. 5 in [6]) clearly indicate a codeposit thickness of  $\sim 30 \mu\text{m}$ , although there is evidence of very high porosity, which leads to a very low effective density. Wampler et al. [5] measured codeposited layer thicknesses of 5–8  $\mu\text{m}$  in this area of the limiter, however, they assumed a density of  $1700 \text{ kg/m}^3$  which is

consistent with other plasma-deposited films, but may not be appropriate for the current high-porosity layers.

## 2.3. D content measurements

As part of the present study, the D content of the codeposited layers was measured by laser thermal desorption. The film specimen was mounted on a holder in a spherical test chamber; see Fig. 1. It was possible to externally rotate the specimen holder such that it could be facing either the laser or the inside of the sphere during  $\text{O}_2$  exposure. A 1064 nm, 40 J neodymium-glass laser (Lumonics Inc. FQ class) with a pulse duration of  $\sim 0.5 \text{ ms}$  was used to heat a small test spot on the specimen,  $\sim 1.3 \text{ mm}$  diameter. 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,  $\sim 1 \text{ J/mm}^2$ , 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. The D content of 1 or more spots on the film was measured after each  $\text{O}_2$  exposure; see Section 2.4. The mass spectrometer was calibrated in situ by a calibrated leak of  $\text{D}_2$ . The quadrupole's relative sensitivity to  $\text{H}_2$  is known from previous calibrations with an  $\text{H}_2$  leak, and the sensitivity to HD is assumed to be the average of the  $\text{H}_2$  and  $\text{D}_2$  sensitivities.

## 2.4. $\text{O}_2$ exposure

$\text{O}_2$  (99.9% purity) exposure was accomplished by backfilling the spherical test chamber to the desired pressure, in this case  $\sim 2100 \text{ Pa}$ . This pressure was maintained constant during the  $\text{O}_2$  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 oxygen. 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 oxygen in the sphere was two orders of magnitude larger than the carbon content of the film specimens, ensuring that the oxygen supply was not limiting the C removal rate. The pumping time constant of the sphere during  $\text{O}_2$  exposure was  $\sim 1\text{--}10 \text{ h}$ . A mass spectrum taken during  $\text{O}_2$  exposure confirmed that  $\text{O}_2$  was the primary species flowing out of the sphere.

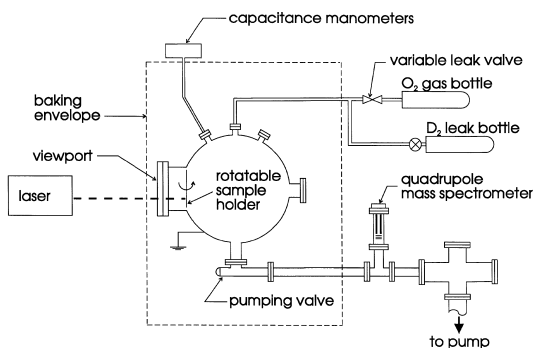


Fig. 1. Schematic of the  $\text{O}_2$  exposure/laser desorption facility.

## 2.5. Mass loss experiments

As there was no visible change in the appearance of the TFTR film even after 99% of the D was removed by O<sub>2</sub> exposure (in the present study, as well as in the study of Causey et al. [2]), mass loss experiments were performed to determine if indeed the carbon content of the films was also being removed. For this measurement, small pieces of tile (frontal area  $\sim 18$  mm<sup>2</sup> and substrate thickness  $\sim 2$  mm) were exposed to O<sub>2</sub> along with some of the larger specimens for laser desorption. In addition, an HPG99 pyrolytic graphite (Union Carbide) reference specimen was also exposed to O<sub>2</sub>. The specimens were weighed before and after exposure on an electronic balance (Ohaus AP 250D), with a sensitivity of 10  $\mu$ g.

## 3. Results and discussion

### 3.1. Laboratory film

Changes in film thickness were estimated based on their deuterium content. This requires knowledge of the film density and the D/C ratio. For the laboratory film, the density was measured by the manufacturer to be  $\sim 2600$  kg/m<sup>3</sup>, and the D/C ratio was chosen to yield a base film thickness of  $\sim 2$   $\mu$ m (the given film nominal thickness). Initial measurements of D content yielded a value of  $\sim 2.6 \times 10^{22}$  D/m<sup>2</sup>, which was used to calculate a D/C ratio of  $\sim 0.1$ . The film thickness as a function of O<sub>2</sub> exposure time at 623 K is shown in Fig. 2. For an oxygen exposure of  $>200$  h, the film thickness was reduced by a little more than a  $\mu$ m, giving an average erosion rate of  $\sim 6.4$  nm/h.

Similar measurements by Wang et al. [4] on a plasma-deposited a-C:D film exposed to air (100 kPa) at 650 K led to an erosion rate of  $\sim 56$  nm/h. The different removal

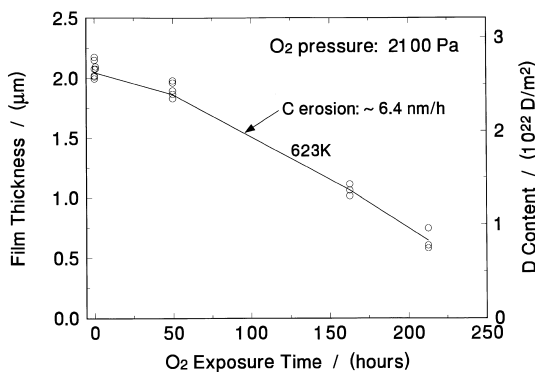


Fig. 2. Film thickness as a function of O<sub>2</sub> exposure time at 623 K for the DIARC laboratory-produced film, as measured by laser desorption.

al rates may be due to different film structures, the slightly higher temperature, as well as the different oxygen concentrations used in the two studies. Since Wang et al. [4] did their experiments in atmospheric air, their O<sub>2</sub> partial pressure was about an order of magnitude higher than the O<sub>2</sub> pressure in our study. In addition, exposure to H<sub>2</sub>O gas (humidity in air) may affect the reactions. Further work is needed to study the dependence of erosion rate on O<sub>2</sub> pressure, as well as the influence of water vapour.

### 3.2. TFTR codeposit

For the TFTR codeposit, the D/C ratio (0.35) was derived from a comparison of laser desorption D-content measurements, and the mass loss measurements (C + D content). Within the error of the mass-loss measurements, consistency was found at all three exposure temperatures (523, 573 and 623 K). Based on the measured mass loss (for the whole film) of  $\sim 160 \pm 20$   $\mu$ g (corresponding to an areal carbon density of  $\sim 4 \times 10^{23}$  C/m<sup>2</sup>), and the 30  $\mu$ m film thickness [6], an effective density of 320 kg/m<sup>3</sup> is estimated. No measurable changes were recorded for the mass of the HPG99 reference specimen, and it is expected that the graphite substrate of the TFTR deposit was also stable against O<sub>2</sub> exposure at these temperatures. (This will be confirmed in future experiments.) The fact that a reasonable value was determined for the D/C ratio, consistent with other tokamak-like films deposited near room temperature, strengthens our confidence in the results. Previous NRA measurements on specimens cut from the same tile [5] found D/C ratios  $\sim 0.2$  and D contents of  $\sim 6 \times 10^{22}$  D/m<sup>2</sup>. Both values are about a factor of two lower than our current measurements, which we consider to be reasonable agreement. Differences in codeposit thickness ( $\sim 5$ – $8$   $\mu$ m in the case of Wampler et al. [5]) are purely due to the different densities assumed for the codeposited layer. In our case, we have used the actual film thickness as shown on the SEM photographs [6] to estimate the density.

Erosion results for the TFTR specimens are shown in Fig. 3 as a function of exposure time. Even at 523 K, the initial erosion rate,  $\sim 4$   $\mu$ m/h, is several orders of magnitude faster than that observed on the laboratory-produced film for O<sub>2</sub> exposure at 623 K ( $<10$  nm/h). At 623 K, the initial removal rate of the TFTR deposit was too fast to be measured by our apparatus,  $>50$   $\mu$ m/h. The removal rate at 573 K was  $\sim 20$   $\mu$ m/h.

By comparison, the C removal rates measured by Wang et al. at 650 K in air [4] for a codeposited layer on an ASDEX-U tile, is about two orders of magnitude lower ( $\sim 0.3$   $\mu$ m/h) than our measurements at 623 K in 2100 Pa O<sub>2</sub>. This discrepancy may be due to the different structure of the codeposits formed in the two fusion devices, or perhaps the impurity content (e.g., the presence of B in the ASDEX-U codeposit) has a significant

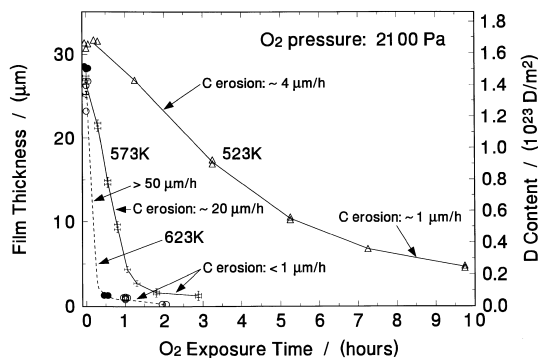


Fig. 3. Film thickness as a function of O<sub>2</sub> exposure time at 523, 573 and 623 K for a TFTR codeposited tile specimens, as measured by laser desorption assuming a constant D/C ratio.

impact on the chemistry. On the other hand, if we infer C erosion rates from the T-content measurements of Causey et al. [2], also for a TFTR tile, their results in air at 623 K would correspond to an erosion rate of ~50 µm/h, in good agreement with our measurements.

A curious feature of the experiments is that even though the codeposits had been nearly completely removed by the O<sub>2</sub> exposure, as indicated by both the D content measurements via laser desorption and mass-loss measurements, their appearance was not visibly altered. It is thought that this may be due to the lower layers of the film being more closely related to the graphite substrate or laboratory-produced films. At 523 and 573 K, the erosion rate (assuming a constant D/C ratio) clearly decreases as the film thickness is reduced, see Fig. 3. Also, for the second hour of O<sub>2</sub> exposure at 623 K, with ~1 µm of the film still remaining, the film removal rate was ~1 µm/h. It might also be possible that the D-content of the films is non-uniform with depth, leading to the observed trends. NRA measurements on a nearby tile do indicate a decrease in D/C ratio with depth (~50%) [5]; however, SIMS depth profiling shows an increase in D concentration with depth (~25%) [6].

#### 4. Conclusions

Erosion rates measured in the current study indicate that codeposited layers in ITER may reasonably be removed by O<sub>2</sub> exposure. Even at the design operating temperatures of 523 K, the removal of codeposited layers of ~100 µm thickness could be achieved in about a day (at a rate of ~4 µm/h). Heating target surfaces to 623 K could lead to much reduced O<sub>2</sub> exposure times. By the same arguments, however, an accidental vacuum loss would result in much of the tritium contained in codeposited layers to be lost [2]. An investigation of film structure, which may lead to an understanding of why such large erosion yields are observed for these films is

underway. The complex surface structure would lead to a much larger effective surface area than for laboratory-deposited films, and hence allow greater oxidation. However, other factors, such as metal contamination may also play a role.

It is noted that thick deposits containing elements such as B and Si, which have been suggested to suppress chemical erosion in tokamaks, may have a significantly reduced reactivity to oxygen. Previous experiments of heating B-doped graphites in air [11] found the materials to be stable to temperatures as high as 1130 K. Thus using dopants to reduce chemical erosion, may have the unwanted effect of making codeposited layers more difficult to remove.

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