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Thermo-oxidation of hard carbon films with tungsten surface impurity

J.W. Davis *, C.G. Hamilton, A.A. Haasz, R.G. Macaulay-Newcombe

Fusion Research Group, University of Toronto Institute for Aerospace Studies, 4925 Dufferin St., Toronto, Ont., Canada, M3H 5T6

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Abstract

The removal of codeposited tritiated carbon films from the next generation of fusion reactors may involve baking in an O_2 environment. Experimental results have indicated that thermo-oxidation can be effective in the removal of such films, however, wide variations have been observed in the oxidation rates of various types of carbon films. In the current experiments, we have investigated the role of metallic impurities by sputter-depositing tungsten onto hard a-C:D films, and exposing them to O_2 gas at 623 K. It was found that rather than catalysing the oxidation of the hydrogenated carbon film, the W deposit tended to inhibit the film removal at this temperature. This suggests that film structure is the predominant factor determining the oxidation rate of tokamak codeposits.

1. Introduction

One of the largest operational and safety concerns in the design of next-generation fusion reactors, such as ITER, is the accumulation of tritium in codeposited films. These layers are formed from the tritium fuel and eroded carbon atoms and hydrocarbons 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 thermal desorption of the hydrogen, and thus such films may incorporate a large quantity of hydrogen. Various techniques have been proposed for the removal of these layers, many of which involve the use of oxygen [1]. The easiest approach is to expose the surfaces to molecular oxygen at elevated temperatures. This has the advantage over plasma techniques in its accessability to shielded components, and not being affected by the magnetic field. However, it must be clearly demonstrated that at the temperatures accessible to future tritium-burning reactors erosion rates will be high enough to remove the type of films which might be produced.

Wide variations exist in the thermo-oxidation rate of codeposited carbon films [2]. In particular, the removal rate at 623 K was found to be on the order of 10^4 times faster for a thick (5 μm) film from TFTR as compared to a laboratory-produced hard a-C:D film [3,4]. It was speculated at the time that both the structure of the tokamak codeposit, and the presence of metallic impurities (∼2%) may have contributed to the enhanced oxidation rate. In another comparison study [5], the oxidation of films deposited in ASDEX-U were compared to the oxidation of a hard a-C:D film at 650 K. The oxidation of the hard carbon film was found to be comparable (within a factor of 2 [2]) to the oxidation of the DIARC film [3], although the oxidation conditions were substantially different; air at 100 kPa (21 kPa O_2 partial pressure) [5] as compared to pure O_2 at 2.1 kPa [3]. The oxidation of the ASDEX-U codeposit, while faster than the hard a-C:D reference film [5], was much slower than the TFTR film reported in [3].

In a previous survey of graphite oxidation [6] we found reported a number of instances where tungsten

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* Corresponding author. Tel.: +1-416 667 7868; fax: +1-416 667 7799.

E-mail address: jwdavis@starfire.utias.utoronto.ca (J.W. Davis).

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contamination was thought to have catalysed the oxidation of graphite, e.g., [7]. Since both carbon and tungsten are materials proposed for plasma-facing components in the next-step fusion reactor ITER [8], we have investigated the effect of tungsten contamination on the oxidation of carbon films by sputter-depositing W onto hard a-C:D film specimens. The oxidation rate of the W-contaminated films was directly compared to the oxidation of uncontaminated specimens.

The use of hard a-C:D films for this study had several motivations. The reproducibility of the films was important when making comparisons with reference specimens. Further, the low porosity means that metallic contamination on the surface will have a greater effect on the chemistry than if the effective surface area was much larger. We also have had previous experience performing oxidation measurements on such films [3].

2. Experiment

2.1. Film specimens

The film specimens were produced by DIARC Technology Inc. of Helsinki, Finland [9]. The deuterium-containing films (D/C content ≈0.1) were made by plasma deposition on a stainless steel substrate. In order for the film to stick to the stainless steel, a W interlayer was first deposited on the substrate. The films were formed in a deuterium background gas and a 60 eV C^+ plasma created by an arc discharge. The substrate temperature was kept below 373 K during the deposition. The film density, as determined by the manufacturer, was 2600 kg/m^3 [9].

In the present experiments we used three a-C:D film specimens produced by DIARC. Surface analysis performed on one of the specimens at the University of Helsinki indicated a film thickness of 3.2 μm and a deuterium content of 8.3 ± 0.4 at.% [10]. The two other specimens had a thickness of 1.8–2.0 μm. All specimens were manufactured under similar conditions, and therefore, were expected to have similar structure and D content.

2.2. Sputter deposition

In the present experiments, the DIARC specimen with 3.2 μm a-C:D film thickness was used as a reference, without W deposition. Tungsten deposition was performed on the two thinner DIARC a-C:D films (1.8–2 μm). The deposition of W onto the specimens was performed by sputtering a W foil with an Ar^+ beam in the UTIAS dual ion beam facility [11]. A 10 keV Ar^+ beam was incident on the W foil at an angle of 45°. The specimens were oriented parallel to the ion beam, and were positioned ∼1 cm away from the W target. X-ray photo-electron spectroscopy (XPS) measurements made subsequent to sputter deposition are shown in Table 1.

Table 1
XPS results for the near-surface of the W-coated DIARC films (XPS probing range is approximately 5 nm)

Specimen	C (at.%)	O (at.%)	W (at.%)	Estimated W coverage
DIARC-10W	61.15	24.25	14.71	8–12 monolayers
DIARC-1.5W	81.90	15.78	2.32	1.3–1.9 monolayers

From the XPS measurements, we infer the presence of 8–12 monolayers of W on DIARC-10W, and 1.3–1.9 monolayers of W on DIARC-1.5W. Analysis of the XPS spectra for C, O and W indicates that most of the W on the surface was in the form of tungsten oxides. While there is a small amount of pure W and/or tungsten carbide, it comprises only about 5–10% of the total W-containing components.

2.3. O_2 exposure at 623 K

Oxygen gas exposure experiments were performed in a bakeable vacuum system by backfilling the vacuum chamber with ∼2.1 kPa of O_2, as measured by a convectron gauge, which was calibrated in situ with a capacitance manometer. This pressure was kept constant throughout the O_2 exposure experiments. External heaters were used to heat the spherical exposure/desorption chamber to the desired temperature of 623 K prior to the O_2 gas backfill. Two copper–constantan thermocouples attached to flanges near the specimen holder were used to measure the temperature throughout the exposure. A schematic of the oxidation/laser desorption facility is shown in Fig. 1. Further details of the experimental procedure are provided in Ref. [4].

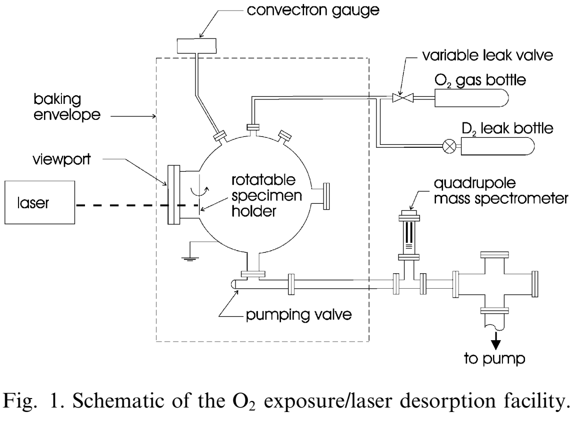

Fig. 1. Schematic of the O_2 exposure/laser desorption facility.

2.4. D-content measurements by laser desorption

Subsequent to the oxygen exposure, the vacuum chamber containing the specimens was evacuated to a base pressure of 10^{-6} Pa. A Lumonics Inc. FQ class 1064 nm, 40 J neodymium-glass laser with $\sim$0.5 ms pulse length was used to heat a $\sim$1.6 mm diameter spot on the specimen, and the released deuterium was measured via residual gas analysis (RGA) using a quadrupole mass spectrometer (QMS) located in the pumping line outside of the baking envelope. QMS signals at $m/e = 3$ and 4 were measured. A single laser pulse, with heat loading of $\sim$1 J/mm^2, was generally sufficient to completely remove the hydrogenated carbon film and the D contained within the film. Smaller amounts of D were released with subsequent laser shots, most likely from the periphery of the spot. Two or three shots were taken at each spot for the results reported here. The D content (i.e., the sum of D in the D_2 and HD molecules observed by RGA) of one or more spots on the film was measured after each exposure to O_2. 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 H_2 and D_2 leaks [12], and the sensitivity to HD is taken to be the average of the H_2 and D_2 sensitivities.

3. Results and discussion

The thermo-oxidation of the two W-coated films and the reference film took place over a 100 h period at 623 K in O_2 gas at 2.1 kPa. As seen in Fig. 2, the D content of the reference specimen decreased by $\approx$40% over 100 h of O_2 exposure. The oxidation rate, estimated to be $\approx 6 \times 10^{-9}$ C/O_2, is very similar to that observed for the oxidation of a similar DIARC film studied earlier [3]. These results are also shown on Fig. 2 for comparison.

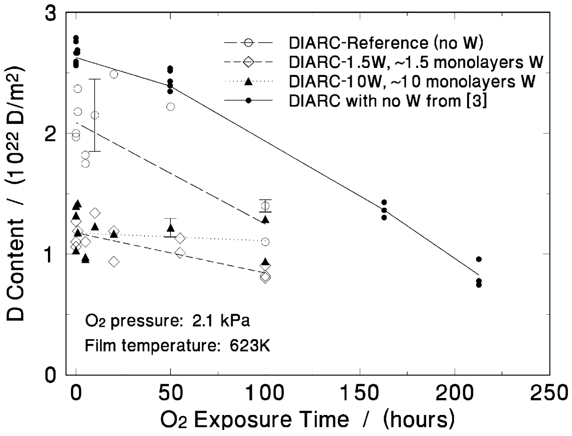

Fig. 2. Deuterium content as a function of O_2 exposure (2.1 kPa) at 623 K. All specimens were produced by DIARC-Technology. The reference specimen had no W deposition, specimens DIARC-1.5W and DIARC-10W had 1.5 and 10 monolayers of W sputter deposited on the surface, respectively. Results from Ref. [3] for a DIARC specimen with no W deposition have been included for comparison.

The initial D content of the two W-coated specimens is similar, and is lower than that of the reference specimen in accordance with the a-C:D film thickness ratio 1.8:3.2 μm. The specimen DIARC-10W, coated with $\sim$10 monolayers of W, showed no significant change in D content during the entire O_2 exposure, implying essentially no erosion of the film. The other W-coated specimen (DIARC-1.5W) did show some decrease in D content, $\approx$30% over 100 h. This gives an oxidation rate of $\approx 2.4 \times 10^{-9}$ C/O_2, more than a factor of two lower than the reference.

It is clear from the results that the deposition of W on the a-C:D film surfaces did not have the expected effect of catalysing the oxidation of the carbon film. On the contrary, oxidation rates appear to have been reduced by the presence of the W, possibly through masking of the film. In the case of DIARC-10W, it appears that the surface roughness of the carbon film is low enough that the W coating is continuous, providing near 100% coverage of the surface. This would explain the suppression of oxidation. For the smaller W deposition (DIARC-1.5W), it is highly unlikely that a continuous W coating was formed, but a significant fraction of the surface may have been covered. The covering of $\approx$60% of the surface would explain the reduction in erosion rates between the DIARC-1.5W and the reference specimens, provided that there was no enhancement of the oxidation process due to the presence of tungsten.

It is possible that tungsten and/or tungsten oxide distributed finely within the a-C:D film might have a larger catalytic effect. This, however, remains to be the subject of a future investigation.

4. Conclusions

The deposition of tungsten onto hard a-C:D films did not appear to enhance the oxidation of the films at 623 K. While the results are not conclusive on their own, they do suggest that film structure is a more important factor in determining the oxidation rate of codeposited films than the presence of metallic surface impurities. Several monolayers of W on the surface, however, will inhibit film oxidation altogether.

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