

Alternative cleaning technique for the removal of carbon deposits

J.A. Ferreira *, F.L. Tabarés, D. Tafalla

Asociación Euratom/Ciemat, 28040 Madrid, Spain

Abstract

High efficiency for the removal of carbon coatings in narrow (1 mm) gaps and carbon films directly exposed has been found in He/O₂ discharges, corresponding to >70% of the yield of directly exposed surfaces. Moreover, the absolute removal rate for the naked films was found to be 12 nm min [J.A. Ferreira, F.L. Tabarés, D. Tafalla, in: 12th ICFRM Conference, Santa Barbara, USA]. This has been associated to the different wall scenarios in the present work, leading to enhanced atomic recycling, of positive effect in the cleaning rate of the carbon films. Also, an alternative cleaning technique was studied, based on glow discharges in H₂/N₂. This is compared with He/O₂. A high cleaning efficiency is also seen, based on the formation of high stable, N–C containing products. Finally, changes in carbon film composition by the addition of B have been identified as responsible for the much higher resistance of doped films against both types of cleaning plasmas.

© 2007 Elsevier B.V. All rights reserved.

PACS: 28.52.Fa; 52.40.Hf; 52.75.Rx

Keywords: Co-deposition; Hydrocarbons; Tritium; Boron compounds

1. Introduction

The use of carbon materials in the high flux area of fusion devices, including ITER divertor for the first phase, is seriously hampered by the formation of co-deposits of carbon and the plasma fuel which are found to migrate to remote areas not reached by the fusion plasma. This problem has triggered the development of a series of in-situ cleaning techniques aimed at the prevention or removal of these

co-deposits or at least to their tritium content [2,3]. Among these, the high temperature oxidation and the glow discharge-driven erosion or isotope interchange have been considered for ITER operation. These techniques have already been tested in some fusion devices, with variable success [4,5]. On the other hand, the possibility of trapping of these co-deposits in gaps; such as those existing between the tiles of the plasma facing components (PFCs) or within the castellated structure of the divertor modules, poses an extra constraint to the available cleaning technique. In this work, the problem of carbon film removal from the gaps existing in castellated structures such as that of the macrobrush

* Corresponding author. Address: Avda. Complutense 22, Ed 6 P2.07 28040 Madrid, Spain.

E-mail address: ja.ferreira@ciemat.es (J.A. Ferreira).

design has been addressed. For that purpose, a metallic structure with gaps of 1 mm and 3 mm depth, in whose bottom is covered by a carbon film layer, was exposed to several cleaning conditions. In particular, glow discharges in He/O₂ mixtures have been tested. The impact of glow discharge parameters and gas mixture on the cleaning efficiency has been investigated by mass spectrometry and thermal desorption spectroscopy.

Since oxygen containing techniques can be incompatible with Be first wall (as it is an oxygen getter) new oxygen free techniques need development. In this paper, a new glow discharge cleaning technique using H₂/N₂ was studied and compared with the He/O₂ mixture. Finally, the effect of changes in the composition of carbon films was tested. The etching characteristics of a-C/B:H and a-C:H films by the glow discharges tested are reported.

2. Experimental set-up

In order to simulate the geometrical constraints of the macrobrush design [1] in respect to the plasma cleaning, a simple metallic structure has been built (Fig. 1). It consists of a Thermocoax wire (SEI 10/100 101 cm 14 Ω), hereafter referred as the wire, of 1 mm diameter, wound at the bottom an aluminum grid structure. The grid is made from a set of eight plates, with dimensions of 1 × 10 cm and 4 mm thick. The plates are bolted to a base plate spaced by 1 mm. A total area of 8 cm² is therefore covered by the wire. This is first coated in a separated reactor. A methane/H₂ mixture is fed into the glow discharge, which creates a-C:H films with good

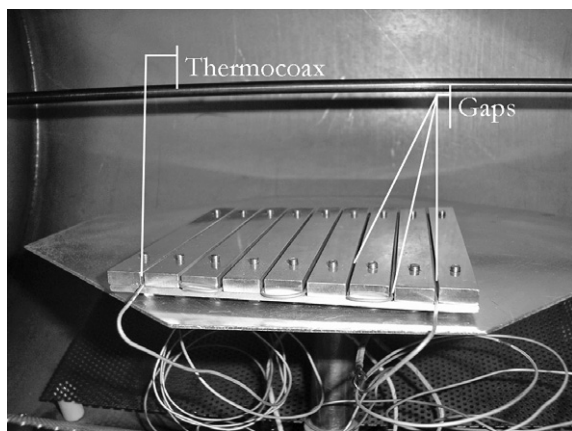


Fig. 1. Oxidation of gaps experimental set-up.

sticking characteristics on the exposed side of the wire. The deposition rate was measured in separated Si samples, by profilometry. A deposition rate of 0.14 nm/s was determined.

After the coating, the wire is installed in a different chamber for cleaning tests. The transfer is made under air. Several blank tests were performed prior to the oxidation conditions in order to validate this technique for the characterization of H film content. This is accomplished through a mass spectrometer (Pfeiffer Vacuum Prisma QMS 200) directly coupled to the cleaning chamber. Temperature is monitored by means of a thermocouple (K type) directly spot-welded to the wire.

Experiments comparing glow discharges of He/O₂ and H₂/N₂ were carried out in a single deposition and treatment chamber. Reactor walls were coated by using a glow discharge in a mixture of He/CH₄ (in the experiments with a-C:H films) and He/*o*-carborane [6] in the experiments with a-C/B:H films. An oven at $T < 100$ °C was used for boronization. After the deposition, the walls were exposed to the different types of glow discharges above referred. Mass spectra were followed during deposition and cleaning by a differentially pumped mass spectrometer.

3. Results

3.1. Cleaning of gaps

After the deposition on the wire, the sample was degassed in vacuum. The obtained mass spectra were used as reference before the exposure to the oxidizing plasma. In Fig. 2, the TDS results for two deposition times (10 and 20 min) are displayed. No significant release of hydrocarbons higher than methane was found. As seen, peaks at 450 and 600 °C were obtained for methane and hydrogen release, respectively. Similar values were obtained in a test experiment with the aluminum grid structure. In-situ calibration of the mass spectrometer for the main desorbed species indicates a 10% yield of methane/H₂, which is very close to the typical value found in the decomposition of hard film having an H/C ratio ~0.4 [2]. Elastic recoil detection (ERD) analysis on the sample confirms this value [7].

The parameters of cleaning plasmas were modified in different runs. A mixture of He and oxygen was always used, but the total pressure (0.67–1.33 Pa) oxygen concentration (5–10%) plasma

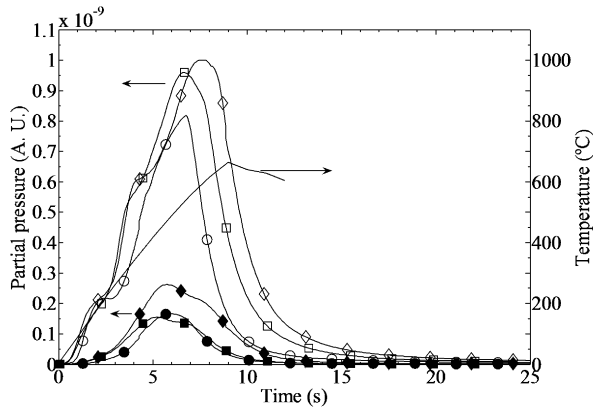


Fig. 2. TDS spectra before exposure to He/O₂ discharge. ● M15 10' deposition + 30' He glow discharge; ○ M2 10' deposition + 30' He glow discharge; ■ M15 10' deposition; □ M2 10' deposition; ◆ M15 20' deposition; and ◇ M2 20' deposition.

current (100–300 mA) and cleaning time (15–30 min) were changed. The sample was maintained at room temperature during the cleaning, but a test at 200 °C was also included. No heating of the wire by the plasma was detected during the cleaning time. Fig. 3 shows a significant reduction on the desorbed amounts of hydrogen and methane after the exposure to the He/O₂ plasma of the shielded wire. The data from the naked wire indicate a high efficiency in carbon removal by the technique, with a minimum rate of 4 nm/min.

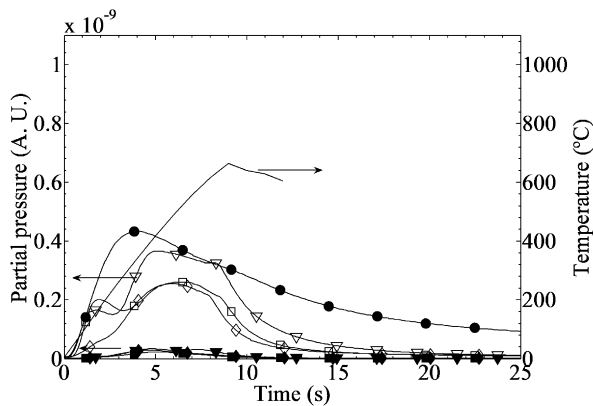


Fig. 3. TDS spectra after exposure to He/O₂ discharge. ● M18 10' deposition + 30' 100 mA, 5 mTorr, 20% O₂ oxidation (nude); ■ M15 10' deposition + 30' 100 mA, 5 mTorr, 20% O₂ oxidation (nude); □ M2 10' deposition + 30' 100 mA, 5 mTorr, 20% O₂ oxidation (nude); ◆ M15 10' deposition + 30' 100 mA, 5 mTorr, 20% O₂ oxidation (200 °C); ◇ M2 10' deposition + 30' 100 mA, 5 mTorr, 20% O₂ oxidation (200 °C); ▼ M15 10' deposition + 30' 100 mA, 10 mTorr, 20% O₂ oxidation; ▽ M2 10' deposition + 30' 100 mA, 10 mTorr, 20% O₂ oxidation.

3.2. Comparison between He/O₂ and H₂/N₂

Next, experiments were carried out in the deposition chamber. To compare the two techniques, He/O₂ and H₂/N₂ glow discharges, they were applied over two identical carbon films of 200 nm. To make these films, a glow discharge of He/CH₄ (35%, 100 mA, 30 min of deposition time) was used. Film thickness was measured by profilometry (in Si samples) yielding a deposition rate of 0.11 nm/s.

He/O₂ treatment was carried out using the optimal conditions obtained in cleaning gaps (20%, 0.667 Pa, 100 mA). Fig. 4 shows the mass evolution during oxidation. The complete elimination of the film takes 1000 s implying a mean erosion rate of 12 nm/min. The main detected products of the film etching are H₂ and CO, but some CO₂ is also formed. Water was also released during the TDS cycle, but no quantitative measurement was possible.

H₂/N₂ treatment was carried out by using the same conditions as in the case of He/O₂ (20%, 0.667 Pa, 100 mA). Fig. 5 shows the results. Masses 27 (HCN and C₂H_x), 26 (HCN and C₂H_x), 25 (C₂H_x) and 52 (C₂N₂) rise in the startup and remain almost constant until the film begins to be fully removed. When this occurs the product distribution changes reducing the contribution of N containing molecules (HCN and C₂N₂) over the hydrocarbon contribution (C₂H_x). The complete film etching takes approximately 3400 s, yielding a mean erosion rate of 3.6 nm/min. The erosion time was found to be proportional to the film thickness. The observed rate might be still improved by optimizing the

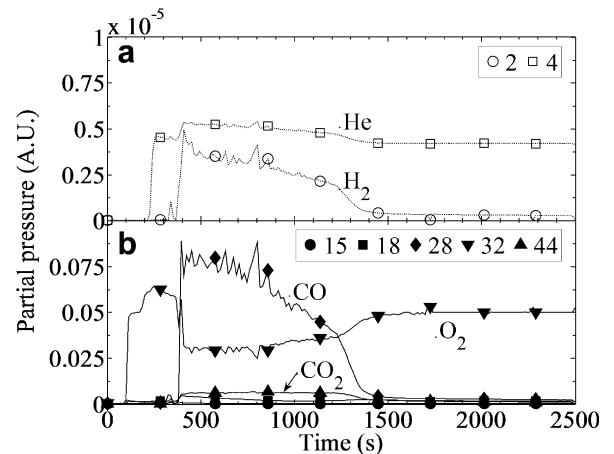


Fig. 4. Oxidation (He/O₂) of a 200 nm depth a-C:H layer. (a) Major masses, and (b) minor masses.

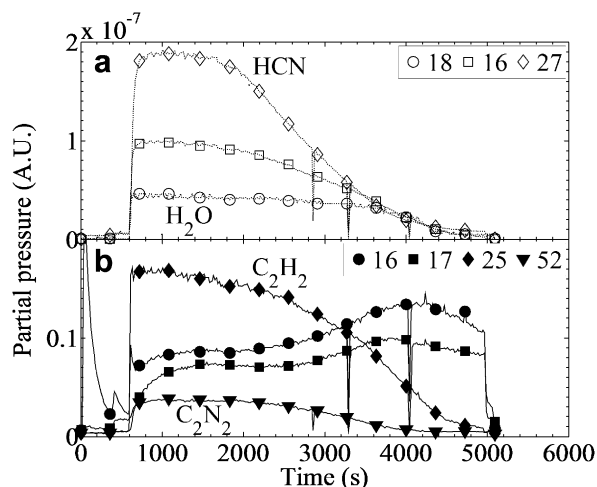


Fig. 5. H₂/N₂ treatment over a 200 nm depth a-C:H layer. (a) Major masses, and (b) minor masses.

conditions of the glow discharge (fraction of N₂, total pressure or current).

H₂/N₂ and He/O₂ techniques were applied to films with different compositions. In particular, an a-C/B:H film was created by using *o*-carborane as precursor [6]. For that purpose *o*-carborane was introduced in a boronization oven and fed into a helium glow discharge in the deposition chamber. Two identical a-C/B:H films were exposed to both techniques (He/O₂ and H₂/N₂) using same conditions as in the previous experiments. These results were compared with that obtained over a-C/H films. Fig. 6 clearly shows a lower reactivity of the a-C/

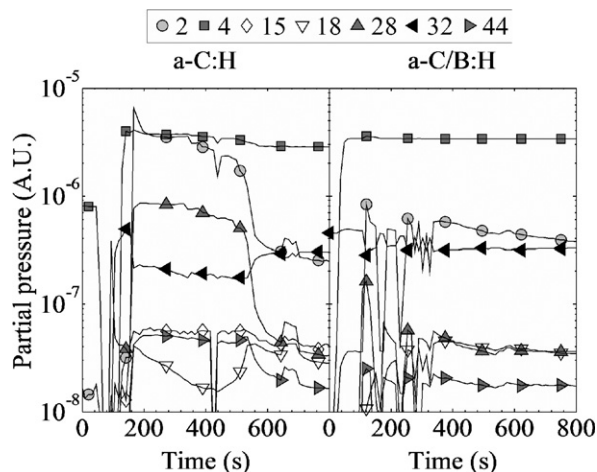


Fig. 6. Comparison of treatment with He/O₂ glow discharge between a-C/B:H and a-C:H layers. On the left treatment over an a-C:H layer, on the right over an a-C/B:H layer.

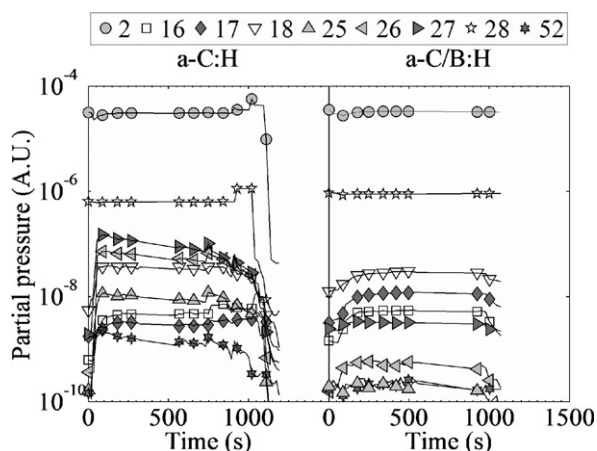


Fig. 7. Comparison of treatment with H₂/N₂ glow discharge between a-C/B:H and a-C:H layers. On the left treatment over a a-C:H layer, on the right over a a-C/B:H layer.

B:H film exposed to He/O₂ glow discharge. Lower concentrations of H₂, CO and CO₂ are obtained in the case of boronized film compared with that of boron-free film. A consumption of O₂ is observed in the a-C:H film during the cleaning but no consumption is observed in a-C/B:H film. No formation of B-bearing molecules was detected through the amu 11 peak. Fig. 7 shows the results of H₂/N₂ treatment. Lower reactivity in a-C/B:H film is observed again. The highest mass in the boron containing layer (except mass 2 and 28) is 18 (water) and no other products are observed. Hydrocarbon film shows similar composition of the product concentration as that displayed in Figs. 4 and 5.

4. Conclusions

A high removal rate (higher than 4.2 nm/min) was observed for the unshielded samples, in contrast with the much slower rates deduced from physical sputtering yield models [8]. Cleaning rates of at least 2/3 of these values are obtained for the films laying on the bottom of the 3 mm deep gap. These facts indicate the important contribution of atomic species in the cleaning mechanism. Atomic concentration could be enhanced in the reported experimental conditions due to the low carbon covered/metal surface ratio.

He/O₂ and H₂/N₂ glow discharge cleaning techniques were tested and compared resulting in a cleaning efficiency of 12 nm/min and 3.6 nm/min, respectively. The possibility of using non-oxidative plasmas for the removal of carbon films at room

temperature will be explored and optimized in future experiments. Finally, boron containing films show much lower reactivity to either of the cleaning techniques here studied, possibly due to conversion from sp^2 to sp^3 hybridization in the presence of B [6].

Acknowledgements

The authors want to thank Dr Gomez-Aleixandre for ERD analysis. This work was partly supported by Dirección General de Investigación Científica y Técnica (DGICYT) under Project FTN2003-08228-C03-01. Also, this work has been strongly motivated by the commitment of the Euro-

pean Task Force on Plasma–Wall Interaction group.

References

- [1] J.A. Ferreira, F.L. Tabarés, D. Tafalla, in: 12th ICFRM Conference, Santa Barbara, USA.
- [2] G. Federici et al., Nucl. Fus. 41 (2001) 1967.
- [3] F.L. Tabarés et al., Plasma Phys. Control. Fus. 46 (2004) B381.
- [4] D. Mueller et al., J. Nucl. Mater. 241–243 (1997) 897.
- [5] V. Philipps et al., in: Proceedings of the 32nd EPS Conference, Tarragona, Spain.
- [6] O.I. Buzhinskij, M.S. Yuri, Fus. Technol. 32 (1997) 1.
- [7] C. Gomez-Aleixandre, private communication.
- [8] B. Landkammer, A. Von Keudell, W. Jacob, J. Nucl. Mater. 264 (1999) 48.