

Study of the chemical etching of carbon surfaces facing argon/hydrogen plasmas in a helicon type reactor

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Abstract—The study of the chemical erosion by atomic hydrogen of graphite in the purpose of characterizing etching and re-deposition growth kinetics is presented. Carbon samples undergo plasma treatment under different time-exposures and gas mixtures at 10 mTorr, determined as the optimal pressure. The etching outcomes are analyzed via mass loss and structure comparison (SEM, micro-Raman spectroscopy) in order to evaluate the impact of the different experimental conditions, *i.e.* pressure, gas mixture, RF power coupling mode and erosion duration.

Index Terms—Atomic hydrogen source, Carbon chemical etching, Carbon dust, Langmuir probe, ITER.

1 INTRODUCTION

IN the path to achieving controlled nuclear fusion as a secure and sustainable energy source, one of the remaining obstacles to overcome is the chemical and physical erosions of the reactor walls by the scrape-off-layer. Indeed, carbon erosion and re-deposition obtained in tokamaks induce important issues such as fusion plasma energy losses by radiation, deconfinement and tritium retention to an unacceptably large amount in the divertor region [1]. A better understanding of the process is essential in order to improve the quality of the carbonaceous compound and limit it from polluting the fusion reaction, especially in ITER.

Laboratory plasmas permit to approach the conditions of tokamak edge plasmas, *i.e.* equivalent electron temperature (< 5 eV) and density ($\sim 10^{12}$ cm⁻³), low pressure, incomplete ionization [2]. On that account, this work focuses on the study of the chemical erosion by atomic hydrogen of different carbon surfaces (graphite and N11 carbon-fiber-composite used in Tore Supra[†]) in the purpose of characterizing erosion (etching and re-deposition growth) kinetics. Therefore the influence of different experimental parameters, such as

pressure, gas mixture, RF power coupling mode and experiment duration, are investigated.

2 EXPERIMENTAL SET-UP

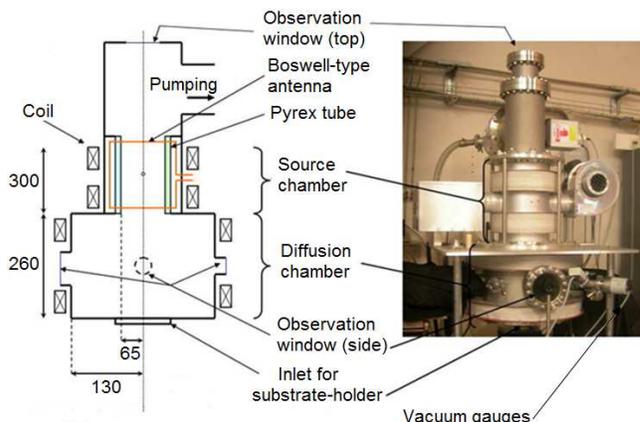


Figure 1: Sketch and photography of the experimental apparatus. Dimensions are given in mm.

Experiments were conducted in a helicon-type reactor presented in Fig. 1. The apparatus is divided in source and diffusion chambers. The former consists of a pyrex tube surrounded by a double saddle type antenna [4] connected to a 13.56 MHz 2 kW RF power supply (P_{RF}) via a Pi matching network. Consequently, the plasma is created in the source chamber and diffuses to the stainless steel

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†. Previous results demonstrated similar results for these two compounds, thus, in this work, only graphite will be studied [3].

diffusion chamber. This transport is influenced by the pressure p inside the vessel.

Two different gas mixtures are used, pure argon and pure hydrogen for physical and chemical etching, respectively. Two sets of copper coils generate downward static magnetic fields up to 200 G in the source chamber (B_s) and up to 100 G in the diffusion one (B_{diff}). Erosion experiments, whose duration t_{exp} may vary, are performed on graphite samples lying on a heating substrate-holder able to reach a temperature T_{sh} of 650 °C.

To study plasma-surface interactions, several diagnostics are carried out for plasma and carbon samples characterizations. Electron density is determined by Langmuir probe measurements via the SmartSoft software from Scientific Systems. The carbon samples are 2×2 cm² squares of 125 μ m thickness extracted from graphite sheets distributed by the company GoodFellow. One sample is used per etching experiment. The erosion outcomes are studied with mass loss, leading to an estimated erosion rate, and structure comparison. The latter is achieved via Scanning Electron Microscopy (SEM). Furthermore, the re-deposited carbon structures are analyzed by means of micro-Raman spectroscopy.

3 RESULTS AND DISCUSSION

3.1 Influence of the pressure

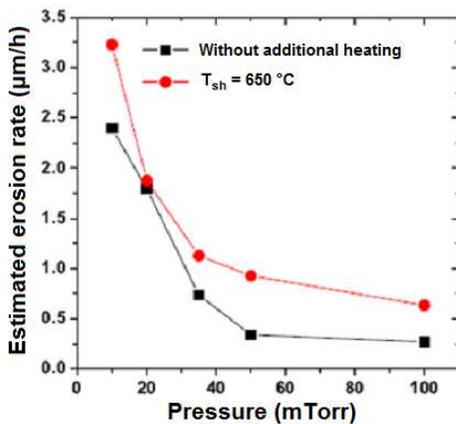


Figure 2: Erosion rate on graphite samples as a function of the pressure p . Pure hydrogen, $P_{RF} = 900$ W, $B_s = 0$ G, $B_{diff} = 100$ G, $t_{exp} = 4$ h, $T_{sh} = 650$ °C. [3]

A preliminary work was achieved in order to obtain the highest erosion rate, thus the strongest atomic hydrogen flux upon the graphite sample. Pressure being one of the main plasma parameters, its effect was examined. As seen in Fig. 2, erosion

rate is inversely proportional to the pressure, the increasing pressure limiting the transport of the plasma. Due to the instability of a pure hydrogen discharge below 10 mTorr, this latter value has been determined as the optimal pressure. Moreover, such a low pressure permits to obtain the helicon mode in our experimental conditions.

One has to notice that, as previously obtained [5], the effect of the substrate-holder temperature is not to neglect, therefore, all experiments were done at $T_{sh} = 650$ °C.

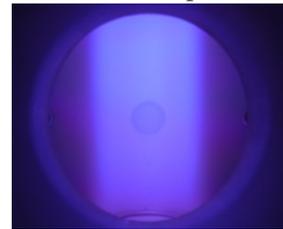
3.1.1 Description



(a) Inductive mode ($B_s = 0$ G), top view.



(b) Helicon mode ($B_s = 120$ G), top view.



(c) Inductive mode, side view.



(d) Helicon mode, side view.

Figure 3: RF modes distinction, plasma pictures from the top and the side windows. Pure argon, $P_{RF} = 1800$ W, $B_{diff} = 100$ G, $p = 10$ mTorr.

The helicon reactor exhibits four modes, including inductive and helicon ones which both present the highest electron density (above 10^{11} cm⁻³ at 900 W). The inductive mode exists for high power, low pressure and $B_s < 20$ G and is described by a very bright and wide plasma column (Fig. 3a and 3c). Helicon mode is characterized by a thin and bright plasma column[‡] and only appears at low pressure and high power for certain (n_e/B_s) couples [6] (Fig. 3b and 3d). The helicon mode was explained by F.F. Chen as the constructive interference between the incident helicon waves and its own reflection [7].

[‡]. The faint peripheral plasma seen in the pictures is due to the TG mode that always coexists with the helicon mode in our experimental conditions.

Additional details about the four available modes can be found in [8].

3.1.2 Physical erosion rate in pure argon

Erosion rate was evaluated in pure argon for the two previously described modes in order to determine the most suited one for carbon etching. One can notice that without any addition of H_2 , the etching is only physical. Experiments lasted for 4 hours (t_{exp}) in the conditions described in the Fig. 3.

The results show an erosion rate of $0.5 \mu\text{m} \cdot \text{h}^{-1}$ in inductive mode and $0.9 \mu\text{m} \cdot \text{h}^{-1}$ in helicon one. The latter mode generating a very confined plasma due to helicon wave propagation, these results seem to show that the helicon column presents very strong electron and ion densities, especially at its very centre. Indeed, a specific and very localized topography can be seen on the sample at a position matching the plasma column centre.

Compared with pure hydrogen plasma which gave $3.2 \mu\text{m} \cdot \text{h}^{-1}$ in the same conditions but less RF power (Fig. 2), argon physical etching is considerably less effective. One has to notice that experiments were conducted without bias voltage on the samples, therefore the latter were at floating potential. In light of these results, the effects of the presence of H_2 in the gas mixture has been analyzed.

3.1.3 Addition of H_2

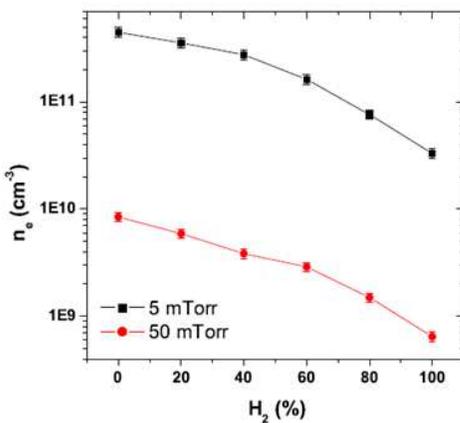


Figure 4: Electron density n_e as a function of H_2 proportion in a Ar/H_2 gas mixture for two different pressures. $P_{RF} = 800 \text{ W}$, $B_s = 0 \text{ G}$, $B_{diff} = 80 \text{ G}$.

The addition of a molecular gas, H_2 , in a pure atomic plasma, Ar , completely depletes the electron density as seen in Fig. 4. It is well known that

electron energy dissipates to excite vibrational and rotational levels of the hydrogen molecule [9].

Such an effect has drastic consequences on the helicon mode. Indeed, the latter is impossible to obtain above a certain hydrogen percentage which could be in line with the assumption that the helicon mode does not appear below an electron density threshold. Taking these results into account, following etching experiments were carried out in inductive mode.

3.2 Chemical erosion kinetics in a pure hydrogen plasma

The mass loss was estimated on graphite samples for different t_{exp} at 1800 W in inductive mode, as depicted in Fig. 5.

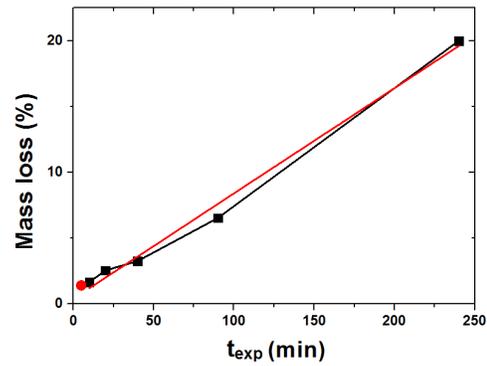
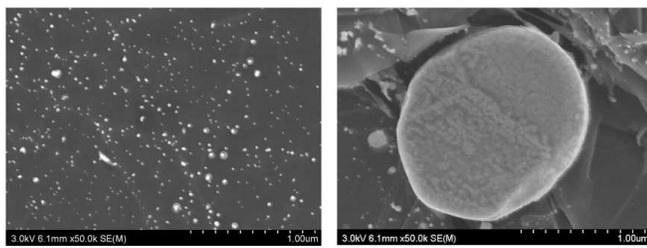


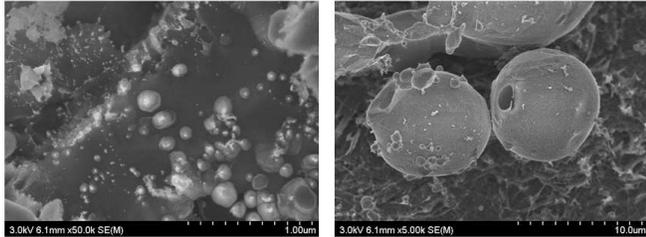
Figure 5: Mass loss percentage on graphite samples as a function of the experiment duration. Pure hydrogen, $P_{RF} = 1800 \text{ W}$, $B_s = 0 \text{ G}$, $B_{diff} = 100 \text{ G}$, $p = 10 \text{ mTorr}$, $T_{sh} = 650 \text{ }^\circ\text{C}$.

At first glance, the mass loss is proportional to the experiment duration which could mean that the two erosion processes, etching and re-deposition, maintain the same contribution to the mass change in time. Calculations from the fit give a constant erosion rate of $6.0 \mu\text{m} \cdot \text{h}^{-1}$ for each sample. This value is in good agreement with the estimated individual values varying from 4.8 to $6.3 \mu\text{m} \cdot \text{h}^{-1}$. The only critical point is seen for $t_{exp} = 5 \text{ min}$ which presents an erosion rate almost twice higher than in other experiments ($10 \mu\text{m} \cdot \text{h}^{-1}$). This phenomenon could be explained by the topography of the untreated samples, the very first minutes of plasma exposure smoothing the sample surface layers leading to a high mass loss and thus, an elevated etching rate. After this smoothing, the bulk of the sample, denser, seems to undergo the etching.

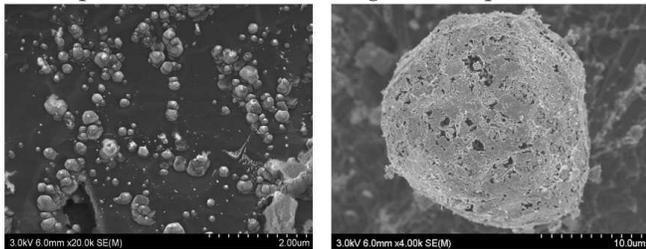
SEM micrographs, as depicted in Fig. 6, exhibits a characteristic topography. After 5 minutes,



(a) $t_{exp} = 5$ min: heaps (zoom: x50k, left) and spherical dust ($\varnothing 1.6 \mu\text{m}$, right) re-deposition.



(b) $t_{exp} = 90$ min: heaps (zoom: x50k, left) and spherical dust ($\varnothing 9 \mu\text{m}$, right) re-deposition.



(c) $t_{exp} = 4$ hour: heaps (zoom: x20k, left) and spherical dust ($\varnothing 21 \mu\text{m}$, right) re-deposition.

Figure 6: SEM micrographs of graphite samples according to their plasma exposure time. Pure hydrogen, $P_{RF} = 1800$ W, $B_s = 0$ G, $B_{diff} = 100$ G, $p = 10$ mTorr, $T_{sh} = 650^\circ\text{C}$.

re-deposition can already be observed (up to $\varnothing 1.6 \mu\text{m}$). The spherical re-deposited structures grow with the exposition time, up to $\varnothing 11 \mu\text{m}$ and $\varnothing 35 \mu\text{m}$ for 90 min and 4 hours, respectively. It seems that the heaps (left pictures in Fig. 6) are created by surface re-deposition. By contrary, the spherical dusts could undergo volume growth in gaseous phase before being deposited on the sample and gain in size by contribution of CH radicals clusters. In any case, one could suggest that radicals resulting from the etching would be deposited preferentially on the already present structures. This could explain why, even though the etching rate is important, massive structures are observed.

Moreover, the latter seem to consist mainly of amorphous carbon. This assumption has been strengthened by the micro-Raman spectrographs which present a clear increase of the disordered

carbon D peaks after plasma treatment.

These porous carbon dusts look similar to those obtained in tokamaks, which are the core of the tritium retention issue.

4 CONCLUSION

The erosion rate of graphite samples was studied varying experimental parameters in order to determine the suited conditions to improve carbon etching, approaching the scrape-off-layer conditions. Re-deposition was analyzed via scanning electron microscope which revealed characteristic structures found on N11 CFC tiles of tokamaks.

It was shown that, in our conditions, the highest etching rate is obtained at 10 mTorr in a hydrogen inductive discharge. However, helicon mode in Ar and Ar/H₂ gas mixtures needs further investigations.

The erosion rate do not seem to have any dependence with the experiment duration. Nonetheless, this parameter has a strong influence on the re-deposition observed via SEM. Additional diagnostics, such as micro-Raman spectroscopy and TEM, should help examine the re-deposited structures detected in hydrogen inductive and argon helicon discharges. High resolution OES, Langmuir probe and TALIF measurements will be performed to characterize plasma species, such as electrons, H, C, C₂, CH and C_xH_y, in order to find correlations and explain fundamental processes responsible of plasma/surface interactions. The aim is to understand these interactions in an attempt to limit them, as well as dust transport, in fusion plasma.

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