

# Investigations of chemical erosion of carbon materials in hydrogen and deuterium low pressure plasmas

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## Abstract

Investigations on chemical erosion of pure and carbide-doped graphite materials were carried out in inductively coupled RF plasmas containing hydrogen, deuterium or a mixture of both in helium. For extrapolations of erosion yields to future fusion devices the relevant particle fluxes have to be known precisely. This was done by several diagnostic techniques. In particular the ion fluxes are determined by an energy mass analyzer. An isotope effect of the ion composition is measured resulting in an enhanced erosion of graphite in deuterium plasmas. Since in fusion plasmas a mixture of deuterium and tritium will interact with the surface, a mixture of hydrogen and deuterium on graphite was investigated as well. In order to reduce erosion yields doping of carbon is under discussion. Therefore, fluence dependent erosion yields of several W-, Ti-, V- and Zr-doped graphite materials are measured and compared with pure graphite.

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## 1. Introduction

Carbon-based materials are used as wall materials in fusion devices. Their advantages are the excellent thermal and mechanical properties, for example the capability to endure high heat loads which occur in the divertor region. On the other hand sputtering and chemical erosion of the carbon materials in hydrogen edge plasmas lead to short component lifetimes and plasma contami-

nation by eroded surface atoms. Redeposited carbon layers can contain high amounts of hydrogen which is critical concerning the usage of tritium. However, carbon is still planned as a divertor material for ITER.

Chemical erosion of carbon depends on surface parameters like temperature and morphology as well as on the incident hydrogen particles. Important parameters are the ion flux, the ion energy and the hydrogen isotope. The presence of neutral atomic hydrogen leads to a synergistic effect which results in an increased erosion yield in comparison to simple superposition of erosion yields due to chemical erosion by hydrogen atoms and by ions only [1]. This behavior can be explained by chemical sputtering [2]. Doping of carbon is a possible way to reduce the strong erosion due to a reduction of the effective carbon surface [1,2].

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For extrapolations of erosion data to future fusion experiments precise knowledge of these parameters is necessary.

In this paper investigations of chemical erosion of pure and doped carbon materials in low pressure hydrogen discharges are carried out. Since such plasmas provide high hydrogen particle fluxes, high fluences ( $\sim 10^{25} \text{ m}^{-2}$ ) can be reached in short periods of time ( $\sim 4 \text{ h}$ ). This means equilibrium conditions of the erosion yield and the morphology can be achieved easily. In addition, the geometry of the experimental setup provides a homogenous plasma above the surface of several centimetres in diameter. An active variation of particle fluxes onto the surface can be achieved by a variation of gas mixture, plasma parameters and by biasing the specimen holder. It has to be kept in mind that bombardment of the surface by particles is always a combination of cold hydrogen atoms and low energy ions where the flux of atoms is higher than the flux of ions.

## 2. Experiment and diagnostics

For systematic investigations of the chemical erosion of several carbon-based materials, a low pressure discharge is used. The inductively coupled RF discharge ( $f = 27.12 \text{ MHz}$ ) operates typically at  $p = 20 \text{ Pa}$  and  $P_{\text{input}} = 250 \text{ W}$  in mixtures of 10% $\text{H}_2/\text{He}$ , 10% $\text{D}_2/\text{He}$  and 5% $\text{H}_2/5\%\text{D}_2/\text{He}$ . An admixture of helium is chosen to increase the electron temperature, electron density and degree of dissociation, i.e. atomic hydrogen density. The samples are placed on a specimen holder in the center of a vacuum chamber of cylindrical geometry. By applying a bias voltage, the energy of the incident ions is varied from 15 eV to 30 eV. The temperature of the specimen is adjusted to 300 K and 500 K by active cooling or heating of the sample.

The properties and producers of the pure graphite and the carbide-doped graphites ( $30 \times 30 \text{ mm}^2$ ) are listed in detail in [3]. As pure graphite the fine-grain graphite type R6650M is used. Carbide-doped graphites are: 4at.% and 2at.% Ti ('TiC4' and 'RGTi91'), 4at.% W ('WC4in' with an inhomogeneous dopant distribution and 'WC4' with a homogeneous dopant distribution), 4at.% V ('VC4') and 4at.% Zr ('ZrC4').

The relevant plasma parameters are determined by several diagnostic techniques. Spatially resolved optical emission spectroscopy OES (Balmer line radiation) yields the atomic hydrogen flux onto the surface [4]. The flux is measured to be  $\Gamma_{\text{H}} = 1.7 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$  for  $\text{H}_2/\text{He}$  discharges and  $\Gamma_{\text{D}} = 2.7 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$  for  $\text{D}_2/\text{He}$  plasmas. In the  $\text{H}_2/\text{D}_2/\text{He}$  mixture the atomic flux is  $\Gamma_{\text{H+D}} = 2.2 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$ . Time resolved measurements of the emission of the CH (CD) band around 431 nm and the emission of the  $\text{C}_2$  Swan band (around 516 nm) lead to a time resolved carbon flux from the

specimen. Absolute values are obtained from calibration with weight loss measurements [4]. For that, the mean value of the spectroscopically determined carbon flux of every time trace is equated with the absolute carbon flux from weight loss. In combination with the incident fluxes, fluence resolved erosion yields are achieved. The electron densities are measured by a Langmuir probe system and are  $n_e = 3.9 \times 10^{16} \text{ m}^{-3}$  in  $\text{H}_2/\text{He}$  plasmas,  $n_e = 5.1 \times 10^{16} \text{ m}^{-3}$  in  $\text{H}_2/\text{D}_2/\text{He}$  plasmas and  $n_e = 6.5 \times 10^{16} \text{ m}^{-3}$  in  $\text{D}_2/\text{He}$  plasmas. From an energy mass analyzer (EMA) ion densities are obtained whereby the extraction hood is placed exactly at the position of the substrate. An absolute calibration of the ion densities is achieved by equating the signals of all hydrogen ion species ( $\text{H}^+$ ,  $\text{H}_2^+$ ,  $\text{H}_3^+$ ) and  $\text{He}^+$  with the electron density. The ion flux is then given by  $\Gamma_{\text{ion}} = n_{\text{ion}} \times v(E_{\text{ion}})/4$ ,  $v(E_{\text{ion}})$  is the velocity of the ions towards the surface obtained from the mean ion energy.

## 3. Results

### 3.1. Ion fluxes

In the present low pressure plasmas the dominating ion species are  $\text{H}^+$ ,  $\text{H}_2^+$ ,  $\text{H}_3^+$  whereby  $\text{He}^+$  and  $\text{HeH}^+$  are also detected. Equivalent species are measured in deuterium. Ion species from impurities are mainly  $\text{H}_3\text{O}^+$  and  $\text{N}_2^+$  with a total contribution of less than 2%. With the presence of a graphite surface in the plasma a broad spectrum of  $\text{C}_x\text{H}_y^+$  ions up to  $X = 10$  is detected with a strong decrease of the intensity for the higher masses. The main species formed through chemical erosion of graphite due to atomic hydrogen are  $\text{C}_x\text{H}_y$  with  $X \leq 3$  [5,6]. The polymerization takes place in the plasma due to heavy particle collisions [7]. Since the total amount of  $\text{C}_x\text{H}_y^+$  and ions of impurities is less than 3% their contribution to the total ion flux can be neglected since the ion energy is low. One of the most relevant parameters for the chemical erosion is the energy of the incident hydrogen ions which is given for all molecular species through the applied bias voltage.

Absolute ion fluxes are shown in Fig. 1 for the different plasmas. In hydrogen plasmas the dominating ion species are  $\text{H}^+$  and  $\text{H}_3^+$  (Fig. 1(a)) with a ratio of  $\text{H}^+/\text{H}_3^+ = 0.9$ . In case of deuterium the amount of the atomic ions increases (Fig. 1(c)) to a ratio of  $\text{D}^+/\text{D}_3^+ = 2.7$ . For the  $\text{H}_2/\text{D}_2$  mixture a ratio of  $(\text{H}^+ + \text{D}^+)/(\text{H}_3^+ + \text{H}_2\text{D}^+ + \text{HD}_2^+ + \text{D}_3^+) = 1.3$  is obtained (Fig. 1(b)). This implies that the energy per atom of the ions increases from hydrogen to deuterium plasmas because the total energy of each ion species is equal. This increases the erosion yield due to chemical sputtering [2] even at the constant ratio of ion flux to neutral atomic hydrogen flux of  $\Gamma_{\text{ion}}/\Gamma_{\text{H}} \approx 0.2$  (Fig. 1). It should be mentioned that the ion composition varies strongly with

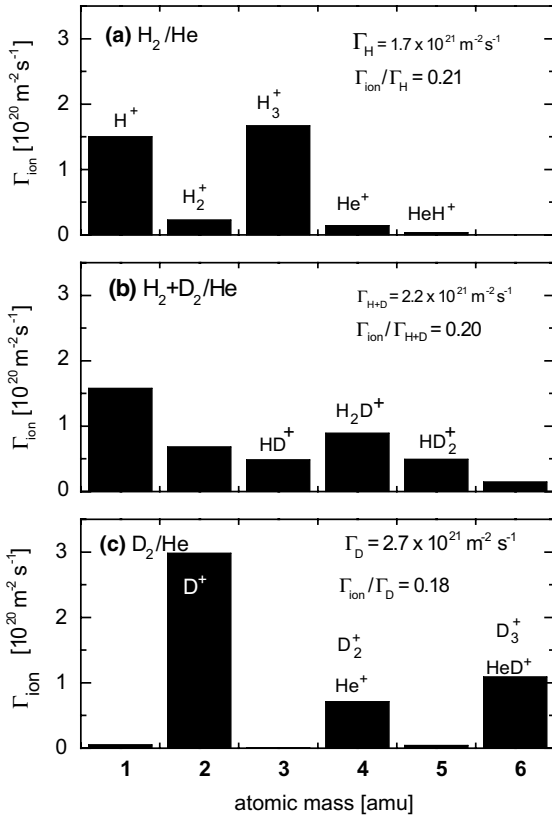


Fig. 1. Ion fluxes in 10% H<sub>2</sub>/He discharges (a), in 5% H<sub>2</sub>/5% D<sub>2</sub>/He discharges (b) and in 10% D<sub>2</sub>/He discharges (c). In part (a) and (c) the appropriate ion species are labeled, whereas only additional possible ions are assigned in (b). The ion energy is  $E_{H^+} = 15\text{ eV}$  in each case.

the percentage of hydrogen in helium for example at 50% H<sub>2</sub>/He the amount of H<sub>3</sub><sup>+</sup> is 95% [8].

### 3.2. Erosion of pure graphite

In general the erosion yield  $Y$  is defined as the ratio of the released carbon flux  $\Gamma_C$  to the incident hydrogen flux  $\Gamma_H$ , i.e.  $Y = \Gamma_C / \Gamma_H$ . In fusion experiments the incident hydrogen particles are ions, whereas in low pressure plasmas cold atoms and low energy ions interact simultaneously with the surface. Therefore, the flux of ions  $\Gamma_{ion}$  (H<sub>x</sub><sup>+</sup>) and thermal hydrogen neutrals  $\Gamma_H$  is taken into account for the erosion yield:

$$Y = \frac{\Gamma_C}{\Gamma_{ion} + \Gamma_H} \quad (1)$$

The presence of chemical sputtering implies that the ratio of  $\Gamma_{ion} / \Gamma_H$  is a relevant parameter as well [2]. The almost constant ratio of  $\Gamma_{ion} / \Gamma_H = 0.2$ , measured in these plasmas, means that the erosion yields would be a factor of five higher if only ions were taken into account.

Fig. 2 shows a comparison of the erosion yields for H<sub>2</sub>/He, H<sub>2</sub>/D<sub>2</sub>/He and D<sub>2</sub>/He plasmas for different ion energies and specimen temperatures. At low ion energies ( $E_{ion} = 15\text{ eV}$ ) and low specimen temperatures ( $T_s = 300\text{ K}$ ) erosion yields of 0.0045 are measured in each plasma (Fig. 2(a)). An increase of the ion energy to 30 eV (Fig. 2(b)) results in an isotope effect, i.e.  $Y(\text{D}_2) : Y(\text{H}_2/\text{D}_2) : Y(\text{H}_2) = 1.9 : 1.6 : 1$ . In comparison to yields at  $E_{ion} = 15\text{ eV}$  H<sub>2</sub>/He plasmas remain constant whereas in D<sub>2</sub>/He plasmas the yield has doubled due to the stronger influence of chemical sputtering. As expected the mixture is in between. The results for higher specimen temperature  $T_s = 500\text{ K}$  (Fig. 2(c) and (d)) show an equivalent behavior with a slight increase in the yields due to thermal processes. Again a dependence on the isotope is observed.

A comparison of measured erosion yield with results from ion beam experiments show a factor of 2 higher yields due to the presence of neutral atomic hydrogen and low energy ions, i.e. chemical sputtering in the plasma [3].

The time resolved release of hydrocarbon species from the surface can be monitored non-invasively by OES. The emission of the CH (CD) Gerö band ( $\sim 431\text{ nm}$ ) and the C<sub>2</sub> Swan band ( $\sim 516\text{ nm}$ ) correlates with the densities of CH (CD) and C<sub>2</sub> which means CH<sub>4</sub> (CD<sub>4</sub>) and C<sub>2</sub>H<sub>y</sub> (C<sub>2</sub>D<sub>y</sub>) respectively [9]. In addition, C<sub>2</sub>H<sub>6</sub> (C<sub>2</sub>D<sub>6</sub>) contributes to CH (CD), what is neglected here ( $n(\text{C}_2\text{H}_6) / n(\text{C}_2\text{H}_y) = 0.1$ ). A higher intensity of the Gerö band and the Swan band is measured in deuterium plasmas which cannot be related to the change of the plasma parameters  $n_e$  and  $T_e$  only. In addition, in deuterium a stronger increase in C<sub>2</sub> emission than in CH (CD) emission is observed. The intensity ratio CD/CH is almost two times higher independent of ion

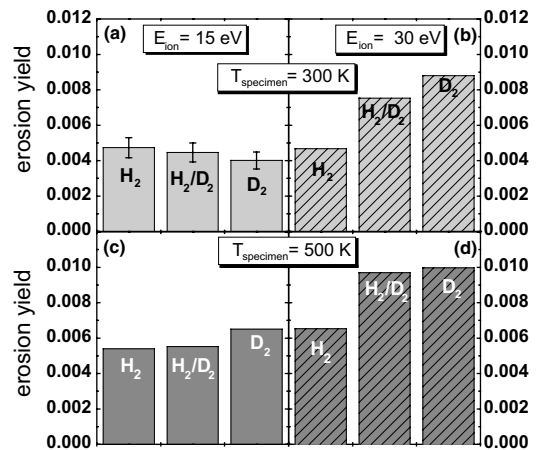


Fig. 2. Total erosion yields  $Y = \Gamma_C / (\Gamma_H + \Gamma_{H^+})$  of graphite for 10% H<sub>2</sub>/He, 5% H<sub>2</sub>/5% D<sub>2</sub>/He and 10% D<sub>2</sub>/He at  $E_{ion} = 15\text{ eV}$  (a and c) and 30 eV (b and d), for  $T_s = 300\text{ K}$  (a and b) and 500 K (c and d).

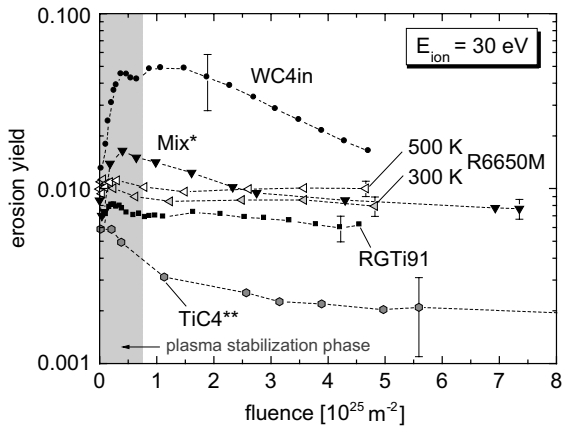


Fig. 3. Fluence dependence of the total erosion yield obtained in 10%  $D_2/He$  plasmas at  $E_{ion} = 30\text{ eV}$  and  $T_s = 300\text{ K}$ . (\*Mix denotes four different specimen VC4, WC4, ZrC4 and a fine-grain graphite placed simultaneously in the plasma, \*\* $E_{ion} = 15\text{ eV}$ .)

energy and substrate temperature. However the intensity ratio  $C_2/CH$  ranges from 0.2 at  $E_{ion} = 15\text{ eV}$  to 0.3 at  $E_{ion} = 30\text{ eV}$ . A temperature variation from  $T_s = 300\text{ K}$  to  $T_s = 500\text{ K}$  causes only a slight increase (2% change in intensity ratio). The ratio  $C_2/(CH + CD)$  in the  $H_2/D_2/He$  mixture is between those of hydrogen and deuterium. In detail, the CD emission is reduced in comparison to deuterium plasmas whereas the CH emission is enhanced in comparison to hydrogen plasmas. Using the correlation of the radiation with the particle densities, it is concluded that more higher hydrocarbons ( $C_2H_y$ ) are released from graphite in deuterium plasmas than in hydrogen plasmas.

Absolute intensities are correlated with the carbon flux (released  $CH_4$  and  $C_2H_y$  particles) with a calibration by weight loss measurements [4]. Time resolved OES measurements provide time resolved erosion yields in a simple way. A constant erosion yield is measured for graphite (R6650M in Fig. 3) which means the erosion yield does not depend on the fluence (fluence =  $(\Gamma_H + \Gamma_{ion}) \times t$ ,  $t_{max} = 4\text{ h}$  corresponds to a fluence of approx.  $4 \times 10^{25}\text{ m}^{-2}$ ). Stable yields are reached after a fluence of  $\sim 8 \times 10^{24}\text{ m}^{-2}$  due to the stabilization phase of the plasma.

### 3.3. Erosion of doped graphites

Since erosion yields of doped graphites vary with time of plasma exposure the fluence dependences for different doped graphites are shown in Fig. 3 for an ion energy of 30 eV (except TiC4 at  $E_{ion} = 15\text{ eV}$ ) in deuterium plasmas. In contrast to pure graphite, doped materials show a decrease of the erosion yield after the stabilization phase of the plasma due to the dopant enrichment

on the surface which results in a reduced effective area of graphite. A weak fluence dependence is observed for Ti-doped graphites (RGTi91 and TiC4). This is expected for RGTi91 since the dopant concentration is low ( $\sim 2\text{ at.}\%$ ) and the grain size is large [3]. At a fluence of  $\sim 3 \times 10^{25}\text{ m}^{-2}$  the fluence dependence vanishes for TiC4, i.e. a steady state erosion seems to be reached. This might be due to the lower ion energy applied in this case. In order to obtain erosion yields under identical conditions exposure of a fine-grain graphite and Zr-, V- and W-doped graphites (ZrC4, VC4 and WC4) was done simultaneously (labeled 'Mix') and show a continuously decreasing erosion yield as it is expected for doped materials. However the net erosion yield is identical for the pure graphite, ZrC4 and VC4 ( $Y = 0.012$ ). This can be explained only by dopant loss during the weight loss measurement process. For WC4 the weight loss results in  $Y = 0.006$ . A very clear dependence of the erosion yield on the fluence shows WC4in which has a strongly inhomogeneous dopant distribution. The high net erosion yield of  $Y \approx 0.040$  can be explained by the drop off of dopant grains as already mentioned above. This results in an overestimation of the carbon flux since the whole weight loss is attributed to graphite. This is supported by investigations with scanning electron microscopy where a strong undercut of the dopant grains appears [3]. In summary, all doped graphites investigated show a reduction of the erosion yield with increasing fluence. Due to dopant grain loss after plasma exposure the net carbon erosion yields are overestimated by weight loss measurements.

## 4. Conclusions

Investigations on chemical erosion of pure and carbide-doped graphite materials by simultaneous bombardment of low energy ions and hydrogen atoms are carried out in low pressure plasmas. The particle bombardment of the surface is always a combination of cold hydrogen atoms ( $T = 600\text{ K}$ ) and low energy ions ( $E_{ion} = 15\text{ eV}$ ,  $30\text{ eV}$ ). An almost constant flux ratio  $\Gamma_{ion}/\Gamma_H = 0.2$  is measured in  $H_2/He$  plasmas,  $H_2/D_2/He$  plasmas and  $D_2/He$  plasmas. Dominant ion species are  $H^+$  and  $H_3^+$  for all isotopes. Since the  $H^+/H_3^+$  ratio is increased in deuterium plasmas the energy per atom is higher which results in enhanced chemical sputtering for deuterium. As expected the erosion yields show an isotope effect depending on the ion energy. A weak dependence on the surface temperature ( $T_s = 300\text{ K}$ ,  $500\text{ K}$ ) is observed. Measurements of the intensity ratio  $C_2/CH$  show that the amount of higher hydrocarbons released from a graphite surface is increased in deuterium plasmas in comparison to hydrogen plasmas. The mixture of hydrogen and deuterium matches the isotope sequence. The combination of weight loss measurements with optical emission spectroscopy

yields the erosion yields as a function of time, and the fluence dependence is obtained. In contrary to pure graphites a reduction of the erosion yield with increasing fluence is measured for doped graphites. A dependence on the dopant is observed. These effects are correlated with an enrichment of dopants reducing the effective graphite surface. Dopant grain loss due to a strong undercut by the plasma may result in an overestimation of the carbon flux and the erosion yield.

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