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Laboratory study of the transport and condensation of hydrocarbon radicals and its consequences for mitigating the tritium inventory in the ITER-FEAT divertor

I.I. Arkhipov [a,*], G. Federici [c], A.E. Gorodetsky [a], C. Ibbott [c], D.A. Komarov [a], A.N. Makhankov [b], A.V. Markin [a], I.V. Mazul [b], R. Tivey [c], A.P. Zakharov [a], R.Kh. Zalavutdinov [a]

[a] *Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky pr. 31, Moscow, 117915, Russian Federation*
[b] *Efremov Institute, St. Petersburg, 189631, Russian Federation*
[c] *ITER-FEAT Garching Joint Work Site, Boltzmannstr. 2, 85748 Garching, Germany*

Abstract

The surface loss probability β of CH_3 radicals at a-C:H surfaces has been determined by analysis of the carbon deposition profiles along a tube flow reactor directly coupled with a methane RF discharge. β is equal to $(1.0 \pm 0.2) \times 10^{-3}$ for a methyl to atomic hydrogen flux ratio of 10:1. β remains the same in the temperature range 300–800 K and decreases slightly between 800 and 1200 K. The deposition rate drops drastically in the range 400–800 K. Above 800 K the carbon deposition is regained. From separate experiments on magnetron sputtering of graphite by D ions, it is inferred that at 300 and 900 kinetic CH_x species react at the C:D surface with the same probability. In contrast, the deposition of thermal C_xH_y radicals decreases by a factor of 25 with a temperature rise from 320 to 400 K, remaining at this low level up to 1000 K. The implications of these results for co-deposition in the ITER-FEAT divertor are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon; Fusion reactor; Redeposition; Growth

1. Introduction

If the ITER-FEAT vertical target is made of carbon-based material [1,2] then the co-deposition of tritium with eroded carbon on the cold surfaces of the divertor is expected to be the main mechanism for tritium retention. Combined erosion analysis shows that 75% of the carbon available for co-deposition builds up at the bottom of the target [2]. The remaining 25%, preferentially in the form of carbon atoms, enters the private flux region and forms carbon films at the liner surfaces. The C_xH_y radicals might be produced due to thermally activated chemical erosion of the films by atomic hydrogen, which is abundant in the divertor atmosphere [3]. A part of these reactive species can pass through the pumping slots and re-deposit on colder surfaces such as the pumping duct and vessel walls, leading to the formation of a tritium inventory.

Recently, an important design modification of the divertor private flux region below the dome was undertaken in the hope of mitigating co-deposition problems [4]. A 'semi-transparent liner' which consists of radiation-cooled tungsten tiles with surface temperatures in the range of 800–1500 K is being considered. The goal is to minimize the amount of tritium trapped in deposits formed on the hot surfaces of the liner and to reduce the co-deposition on the colder surfaces behind the liner. A database on surface reactions of reactive species can

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[*] Corresponding author. Tel.: +7-095 330 2192; fax: +7-095 334 8531.
E-mail address: arkhipov@ipc.rssi.ru (I.I. Arkhipov).

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provide key input parameters for the design of such a semi-transparent liner.

The aim of this study is to reveal the influence of temperature and atomic hydrogen on the transport and condensation of hydrocarbon radicals. Inductively coupled RF discharge in methane and magnetron sputtering of graphite in deuterium are used for the production of reactive species. Based on these results, suggestions for a hot liner design are discussed.

2. Tube experiment

The so-called 'stream technique' was used to study the interaction of hydrocarbon radicals with hot surface [5,6]. Basically, a stream of neutral plasma products was passed through a cylindrical tube reactor. The reactive species were lost at the tube walls via the formation of a-C:H layers. The surface loss probability β of the radicals was determined by the analysis of the deposition profile along the tube using a simple model for the reaction loss kinetics of reactive particles on cylindrical reactor walls. With a knowledge of this β value, it was possible to identify the hydrocarbon radical forming the deposit. The details of this approach as well as techniques of the film characterization are described in [7].

The experimental setup consisted of a cylindrical quartz tube directly coupled to an RF discharge (Fig. 1). The tube had a diameter of 2 cm and a length of 100 cm and was pumped at one end. At the opposite end methane was introduced at a pressure of 30 Pa. In all experiments, methane flow rate was 13.7 sccm, which corresponds to a linear flow velocity of 280 cm/s and a particle residence time (for non-reactive species) in the deposition area (60 cm length) of about 0.2 s. The radial diffusion time was equal to 0.3 ms. So, on average, each particle suffered about 700 collisions with the wall during the residence time in the deposition area. The gas passed an inductively coupled RF glow discharge with the following parameters: frequency 13.56 MHz, specific power ~0.1 W/cm^3. The plasma was limited by a metal grid at a floating potential. The grid size was 0.05×0.05 cm^2. In the afterglow area behind the grid the deposition rate dropped more than one order of the magnitude on a length of about 1–2 cm. Therefore, one can conclude that via the grid only thermal neutral hydrocarbon radicals and stable molecules emanating from the plasma can pass. The central section of the deposition area (15 cm of length) can be heated via an external cylindrical furnace up to a temperature of 1200 K. The temperature distribution along the tube was measured by a thermocouple with an accuracy of 10 K.

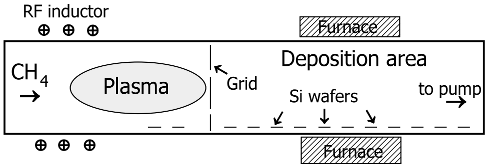

Fig. 1. Schematic cross section of the gas flow reactor.

The deposition rate of carbon layers at different positions along the tube was normalized to the deposition rate in the discharge region and is shown in Fig. 2. The experiments were performed at room temperature (300 K) and at 400, 800 and 1200 K in the furnace centre. Note that a part of the experimental points at 300 K fit an exponential decay curve (solid line) obtained from model [7]. This suggests that only one precursor was responsible for film growth in the area. For this case, β is equal to $(1.0 \pm 0.2) \times 10^{-3}$. For a methane RF discharge, it is reasonable to assume that the methyl radical was one of the dominant radicals leading to a $\beta = 10^{-3}$ [8–12] in the afterglow region.

The deposition profiles at elevated temperatures show that above 380 K a strong decrease (10–100 times) of the deposition rate can be observed. However, at temperatures above 800 K the carbon deposition rate

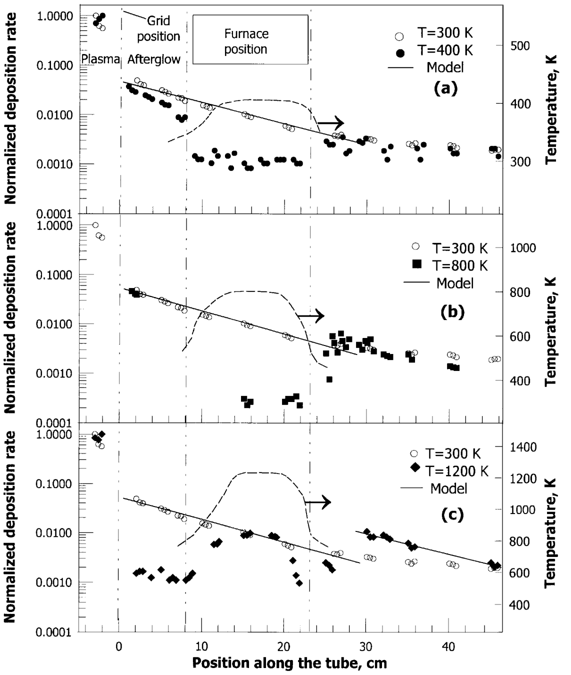

Fig. 2. Normalized carbon deposition rate as a function of position along the quartz flow reactor for three different temperatures of the furnace: (a) 400 K, (b) 800 K and (c) 1200 K. For comparison, the deposition rate at room temperature (300 K) is shown. The solid lines denote the modeling of a part of the deposition profile at 300 K (a, b, c) and 1200 K (c) for $\beta = 10^{-3}$. The dashed lines correspond to distribution of temperature along the tube.

increased again and reached, at about 1200 K, the magnitude of the 300 K deposition level. This temperature dependence of the net deposition rate is thought to be due to the temperature-dependent erosion by atomic hydrogen [13]. Experimental data obtained in [7] on H-induced etching of specially prepared carbon films under the same deposition conditions support this assumption. According to our estimation, the methyl to atomic hydrogen flux ratio for the furnace centre position is about 10:1.

A comparison of deposition profiles obtained at 300, 400 and 800 K shows that the deposition rate in the relatively cold (300 K) area behind the furnace was unchanged (see Figs. 2(a) and (b)). This shows that a heated region does not affect the transport of radicals through the tube. In other words the surface loss probability β is unchanged in the temperature range 300–800 K. As the sticking probability s of reactive species between 400 and 800 K is very small due to re-etching, β is equal to $s + \gamma \approx \gamma \approx 10^{-3}$ (where γ is the recombination probability of impinging radicals into non-reactive volatile molecules).

The carbon deposition rate behind the furnace heated up to 1200 K was seen to increase (Fig. 2(c)). As these experimental points fit the curve (solid line) corresponding to $\beta = 10^{-3}$, it is reasonable to consider that methyl radicals were responsible for the film growth in the area once again. Keeping in mind that surface loss probability β was unchanged between 300 and 800 K this result can be understood as decreasing β in the temperature range 800–1200 K (in our estimation from 10^{-3} to about 6×10^{-4}).

3. Magnetron experiment

The experimental details of the magnetron discharge can be found in [14]. Briefly, a graphite target of 14 cm in diameter was used as a cathode and the grounded chamber walls were used as an anode of the discharge (Fig. 3). Deuterium was used as a working gas. In the present paper, we discuss the results of two sets of experiments. A discharge voltage of 400 V and a discharge current of 1 A were used for both experiments.

In Set A, (Fig. 3(a)) the cathode temperature was maintained at 320 K. The discharge pressure was kept at 0.1 Pa. The substrate being at floating potential was placed 7 cm above the cathode center. This distance is comparable to the mean free path of the gas molecules. Thereby, most of the sputtered species leaving the cathode impinged onto the substrate with an energy of a few electron volts [8,15]. Further plasma ions were accelerated in the cathode sheath and neutralized and reflected at the cathode, and reached the substrate with energies in a range from 0 to about 200 eV [14]. Finally, the substrate was also bombarded with plasma ions accelerated in the substrate sheath with energies of ~20 eV at maximum [14].

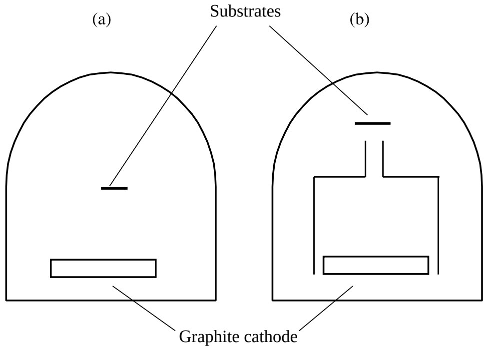

Fig. 3. Schematic of the experimental setups for production of (a) kinetic CH_x species and (b) thermal C_xH_y radicals.

In Set B, the plasma was confined by an additional chamber (Fig. 3(b)). The cathode and the chamber walls were kept at temperatures of 800 and 600 K, respectively. In this case the cathode produced not only fast neutrals via sputtering as in Set A, but also emitted methane, the predominant constituent of chemical erosion of graphite with D ions [15]. Furthermore, higher hydrocarbons were generated through re-erosion of the a-C:D films grown on the chamber walls with thermal D atoms [3]. Plasma products diffused through a 1 cm aperture to the main chamber. In order to come close to conditions where the films grow from thermal hydrocarbon radicals, a 3.6 cm long tube with a diameter of 1.6 cm and heated to a temperature of 600 K was mounted in front of the substrate. This significantly lowered the plasma density near the substrate, as evident from electric probe measurements [14]. In addition, the discharge was ignited at a relatively high pressure of ~1 Pa, so that any energetic particles reflected at the cathode underwent many collisions in gas phase before they reached the substrate. Summarizing, film deposition on the substrate occurs from kinetic CH_x species in Set A and from thermal C_xH_y radicals in Set B.

Carbon deposits on W substrates exposed for 0.5 h at different substrate temperatures are shown in Table 1. For Set A, only a slight decrease in the deposition rate is seen at 400 K as compared to that at 300 K. At 500 K the deposition rate is 30 times lower than at 300 K, but

Table 1

Amount of carbon (10^{21} C atoms/m^2) deposited in two sets of experiments at the magnetron, Set A (Fig. 3(a)) and Set B (Fig. 3(b)), onto W substrate for 0.5 h at different temperatures

T (K)	320	370	400	500	600	900	1100
Set A	28	–	23	1	–	38	–
Set B	5	2	⩽0.2	–	⩽0.2	–	⩽0.2

at 900 K, it is the same as at 300 K. In contrast, only a slight increase of the substrate temperature in Set B from 320 to 400 K leads to at least a 25-fold decrease in deposition rate. In addition, the deposition rate remains small also at elevated temperatures.

In the case of C:H film production using hydrocarbon plasmas, the deposition rate can be modeled by the temperature-dependent processes of (1) film growth via sticking of carbon carrying ions and radicals and (2) film erosion mainly by thermal hydrogen atoms abundant in the plasma [16]. For the particular case of the ECR methane plasma von Keudell and Jacob [17] suggested a temperature-independent growth mechanism up to 600 K. A drop in deposition rate observed in the range 300–600 K was explained solely by a fast increase in erosion yield. Based on this approach and having in mind the fact that the erosion yield decreases remarkably above 600 K [3] the variation of deposition rate found in experiments of Set A can be understood if it is suggested that kinetic CH_x species stick effectively at the growing C:D surface in the complete temperature range tested, and only the re-etching causes the overall variation of deposition rate. If so, the very low deposition observed in Set B in the range of 400–1100 K indicates clearly a negligible contribution of fast particles to film growth in this case. However any conclusion on the temperature dependence of the sticking of thermal C_xH_y radicals remains difficult. We can only point out that, as opposed to kinetic species, the sticking coefficient of thermal radicals present in Set B is small at elevated temperatures.

4. Discussion and application to ITER-FEAT

In both types of experiments presented in this paper, carbon deposition in the appropriate temperature range as proposed for the ITER-FEAT divertor private region is studied. In general, they both present similar results, which indicate that the deposition rate drops drastically beginning at about 400 K. Therefore, in our opinion, the operating temperature of the pumping duct should be at least 400 K.

It was shown in the tube experiment that the low net deposition rate of methyl radicals might be caused by the re-erosion of the growing carbon layers by atomic hydrogen. Because the surface loss probability of the radicals is quite small (about 10^{-3} at $CH_3:H = 10:1$) and was unchanged at 400 K, they can penetrate deeply into the pumping duct. If the number of radical–wall collisions is small ($<10^3$), the methyl radicals might pass the heated pumping duct and reach the cryopump.

No direct identification of the growth precursor in the magnetron experiment was possible. Nevertheless, it might be proposed that high (>0.1) sticking coefficient radicals like C_2H and C_2H_3 are produced in our magnetron plasma similar to the hydrocarbon plasmas of the ECR discharge [18]. If the low deposition rate at 400 K is a result of re-erosion it is reasonable to assume that the concentration of these particles will strongly decrease downstream along the pumping duct, because the re-eroded species are mainly methyl radicals [3]. Alternatively, the low deposition rate might be explained by a decrease of the sticking probability of the radicals. In this case a significant transport of the radicals through the pumping duct is possible. To prevent the transport it will be necessary to place a cold <320 K catcher plate below the hot liner. This plate could then be heated to release any co-deposited tritium.

It is significant that the deposition rate of kinetic CH_x species in the magnetron experiment as well as thermal CH_3 radicals in the tube experiment is regained above 1000 K to a level close to 300 K deposition. This fact can be explained by the very low erosion yield of growing carbon films by thermal hydrogen atoms ($\sim 10^{-4}$ at 900 K for graphite [3]). Thus the hot liner might collect a part of the incoming hydrocarbon flux thereby mitigating the co-deposition problem in the pumping duct.

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