A-C:H Film Removal in H_2 and H_2/N_2O Glow and Afterglow Discharge

R. Kh. Zalavutdinov 1), A. E. Gorodetsky 1), V. L. Bukhovets 1), A. P. Zakharov 1),
I. V Mazul 2)

1) A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, RF
2) D.V. Efremov Institute of Electrophysical Apparatus, St.-Petersburg, RF

e-mail contact of main author: rinad@ipc.rssi.ru

Abstract. In the experiments a stream technique has been used and it has been shown that the main product of a-C:H film gasification in an afterglow region of a direct current glow discharge was methane (hydrogen discharge). A hard a-C:H film erosion rate in the afterglow region decreased exponentially with distance from an atomic hydrogen source. The disadvantage of the hydrogen discharge is low erosion yields at 320-420 K ($Y \approx 0.001$ at. C/at. H, i.e., erosion rate is lower than 0.2 nm/min). For efficiency enhancement of hydrocarbon film removal in the afterglow region an H_2 (40 Pa)/N_2O (3-7 Pa) mixture containing oxygen component has been proposed. In such medium activated by the discharge the main erosion film products were CO and CO_2. The erosion rate of the samples located at distance of 11 cm from plasma was 2 nm/min at 420 K. The addition of N_2O in H_2/CH_4 direct current glow discharge suppressed C:H film deposition completely. The technique suggested is one of possible variants of an effective gas-discharge technology for hydrocarbon deposit removal from the remote construction parts of ITER plasma.

1. Introduction

In ITER project CFC composites are proposed as divertor targets for exhaust D/T plasma with total surface of ~55 m^2 and weight of ~1 ton [1]. The main advantage of the CFC composites is an ability to take a high heat load (about 10 MW/m^2) and the serious shortcoming is chemical erosion susceptibility under interaction with hydrogen plasma when hydrocarbon molecules and radicals are formed.

Experiments on current tokamaks have shown that deposited hydrocarbon films contain a large amount of D and T with a ratio $(D+T)/(D+T+C) \approx 0.5$. Carbon and hydrogen isotopes joint deposition may be a principal mechanism of “dead” tritium retention which content has not to exceed 350 g. This tritium value in the lower section of main tokamak vessel will be reached after five hundred discharges each 400 s duration [2]. Thereupon, it is necessary to develop both methods for chemical erosion decreasing of carbon materials and techniques for T-C film removing [3, 4].

The aim of the paper is development of an effective gas-discharge technology for removal of hydrocarbon deposits from remote construction parts of ITER plasma. In the paper there is considered erosion of hard hydrocarbon films which are gasified with difficulty comparing with soft ones. Experiments were performed both in a direct current glow discharge and afterglow region using H_2 or H_2/N_2O mixture.

2. Experimental

A direct current glow discharge (DCGD) with a hollow cathode in H_2 or H_2/N_2O mixture was used as source of atomic hydrogen and chemically active species (nitrogen and oxygen) capable to form gaseous carbon compounds. In a stream technique as a chemical reactor we used a quartz tube 110 cm long (inner diameter of 1.9 cm) with two soldered quartz tubes of the same diameter and each 25 cm in length both located in a horizontal plane (Fig. 1). The H_2 and N_2O flows were set by controllers (1) and (2) in the ranges 1-14 and 0.4-1 sccm, respectively, with an accuracy of 0.01 sccm. After the controllers the flows entered the discharge zone through the hollow cathode (15 cm length, 1 cm radius) made from stainless steel (SS) and cooled by running water. A connection circuit between the hollow cathode and the grounded anode (sometimes we used a hollow anode) permitted to achieve a stable discharge at pressures up to 50 Pa and currents of 5-50 mA. The lengths of a positive column and afterglow zone were each 70 cm. A part of the afterglow region of the 50 cm long could be heated up to 1000 K by an external cylindrical furnace with a length of 15 cm. In the gap between the furnace and tube a thermocouple was placed. The pressure in the reactor was regulated by means of a valve (5) located at the tube outlet. A Pirani gauge (PG3) was placed at the pumping tube end. A small part of gas mixture was extracted for analysis in a differentially pumped quadrupole mass-spectrometer connected to the reactor by a leak valve (4). The reactor was pumped down to a pressure of 0.1 Pa before starting the experiment. A rate of inleakage of air did not exceed 3×10^{-3} sccm at limiting background better 0.1 Pa.

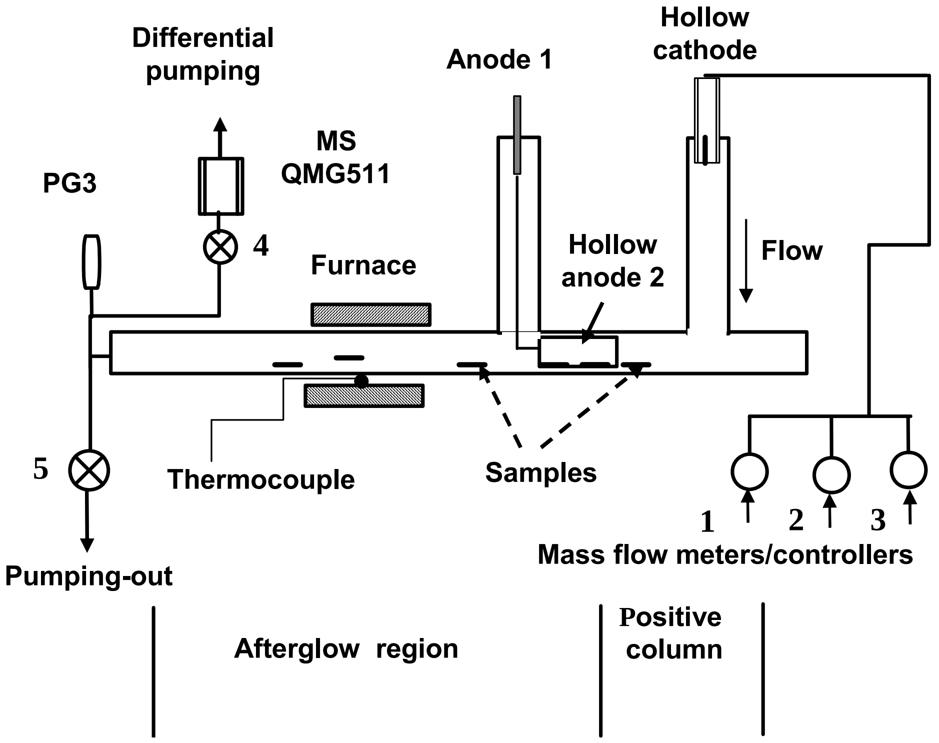


FIG. 1. Scheme of setup for studying of a-C:H film erosion. 1, 2, 3, - controllers. 4, 5 - valves.

The discharge was limited by a special anode arrangement in the lateral quartz tube from the main tube (anode 1) or a hollow SS anode (anode 2) in the main tube (Fig. 1). The average energy of ions impinging the cathode did not exceed 100 eV at cathode drop of 350 V. The plasma column consisted as a rule of the set of the immobile strata (laminated discharge) formed in the gas moved with a velocity 1-5 m/s. The average energy of ions impinging the tube wall in the positive column region did not exceed 10 eV.

Hard diamond-like a-C:H films (600-800 nm thick) deposited on Mo or Si substrates have been used for carbon erosion study [5]. The films in large quantities are formed on inner divertor surfaces and are gasified very hardly [6]. A carbon erosion rate was measured by two methods: weighing (accuracy 10^{-7} g) and electron probe microanalysis (EPMA) (accuracy 10^{16} at.C/cm^2, $2\cdot10^{-7}$ g/cm^2). An average density of the a-C:H films determined by weighing and thickness measuring was equal to 1.83±0.05 g/cm^3. Products of a-C:H film erosion have been studied by a differentially pumped quadrupole mass-spectrometer.

3. Results and discussion

3.1. A-C:H Film Removal in H_2 Glow and Afterglow Discharge

Experimental data on H atoms interaction with different carbon materials one can summarize using a carbon erosion coefficient, *Y*, (C at./H at.) which means the number of carbon atoms sputtered per one incident hydrogen atom (but not ion) [7, 8]. *Y* increases with temperature an order of magnitude reaching the values ~0.01 and ~0.1 C at./H at. for hard and soft a-C:H films, respectively, at 650 K (Fig. 2). At further temperature increasing *Y* decreases due to parallel H atom recombination. *Y* increases in a row: diamond, graphite, hard and soft a-C:H films. As follows from Fig. 2, the more hydrogen is contained in solid carbon the higher is its chemical erosion coefficient in regard to hydrogen atom incident flux [9]. Such *Y* change provides the prerequisites for development of hydrocarbon deposit removal technique without essential impact directly on carbon divertor targets.

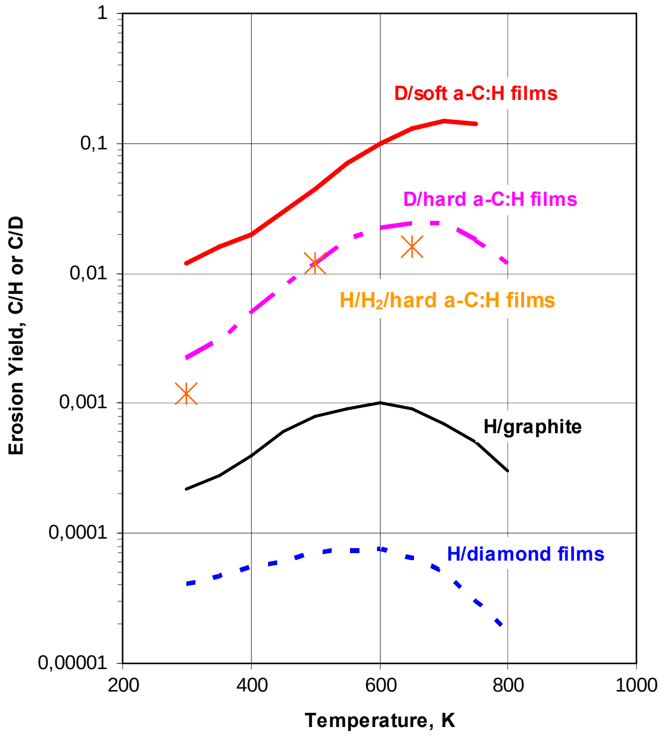


FIG. 2. Erosion yield, Y, (C at./H at.) vs temperature for different carbon materials under interaction with H(D) atoms [9]. ✳ - our experimental data.

The usage of hydrogen atom stream source to study solid carbon erosion in moving H/H_2 mixture was necessary to reveal the correlation between the data obtained by beam techniques [10] and data obtaining in gas-dynamic flow. For that it was performed the comparative gasification of a-C:H films made in IPP (Garching, Germany) and IPCE RAS (Moscow, Russia). For the former ones, *Y* was 0.02 at 650 K [10]. The film erosion rate for both film types was identical that allowed to make conclusion about similarity of their structures and approximate equality of hydrogen concentration.
At 320 K the erosion rate (~1.8 nm/min) directly in the discharge was almost reasonable for

technical applications and increased 20 times at 650 K (Fig. 3). In the afterglow zone the erosion rate decreased as exp (-*x*/*L*) where *L* = 3-4 cm is a transport length. In the temperature range 300-420 K that is accessible for ITER preventive procedures the erosion rate in the afterglow zone turned out to be lower than 0.2 nm/min.

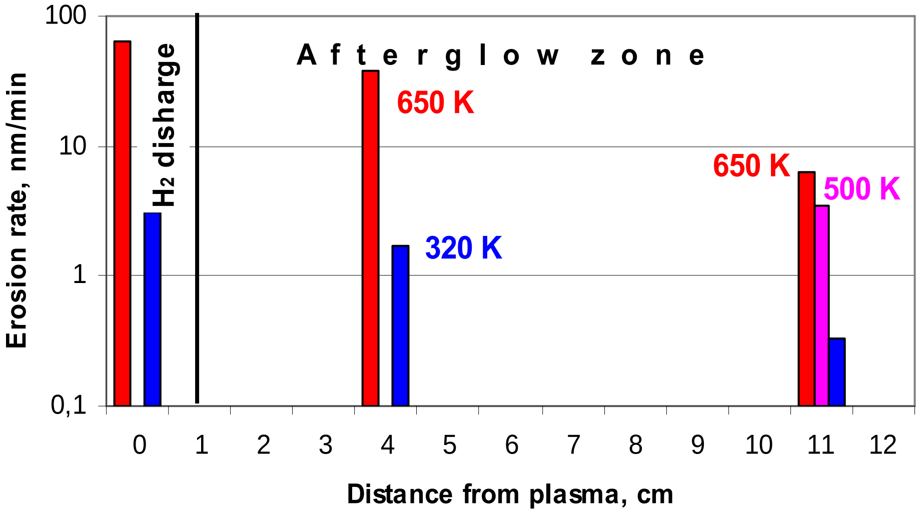


FIG. 3. Hard a-C:H film erosion rates in the H_2 direct current glow discharge (23 mA, 0.6 kV). Hydrogen pressure is 40 Pa, flow rate is 7 sccm and flow velocity is 1.15 m/s.

Mass-spectrometric measurements have indicated that methane (CH_4) was the main erosion product at sample location in the afterglow region at 320-650 K. Total ethane and ethylene concentration in erosion products did not exceed 3%. Methane yield and a-C:H film erosion rate (650 K) at distance of 11 cm from the positive column increased linearly at discharge current increase from 5 up to 50 mA or with increase of H atom generation efficiency. This conclusion was made up both from CH_3 (15 amu) amplitude measurements during erosion and EPMA and film weighing data before and after erosion experiments. Methane yield and erosion rate were proportional to atomic hydrogen flow towards the hydrocarbon film surface that corresponded to the first order of gasification reaction. We assumed that in the afterglow zone, where thermalized atomic hydrogen was the main etching agent, the film gasification proceeded through successive reactions of H atom addition to surface complex CH_y accoding to reaction:

$$CH_y + H = CH_{y+1},$$

where y = 1, 2, 3. In this reaction raw one of three stages is determinative one [8].

It should be noted that the preferable CH_4 formation during a-C:H film erosion was observed only in the reaction of carbon with the thermal H atoms. If the a-C:H films were in contact with hydrogen plasma near the cathode, in which the H ion energy was about 30-100 eV, C_2H_x and C_3H_x hydrocarbons appeared in an erosion product spectrum.

The technique of redeposited a-C:H film removal from remote parts of ITER divertor plasma based on interaction of carbon with H/H_2 mixture has several positive peculiarities: i) it can use deuterium which is one of nuclear fuel components; ii) methane is the erosion product which is very suitable gas for further processing and tritium separation; iii) there is gasification selectivity regarding different carbon forms; iiii) there is also local gasification selectivity at possibility of temperature increase of separate technical units of large plasma device. The shortcomings of H/H_2 mixture as glow discharge working gas are the rather small values of the erosion coefficients in the temperature range 320-420 K (*Y* of scale 0.001 C at./H at.) and minor transport length *L* in the afterglow zone (of scale 3-4 cm in quartz tube of 2 cm in diameter). These shortcomings can be overcome when effective H atom sources will be constructed.

3.2. A-C:H Film Removal in H_2/N_2O Afterglow Discharge

For efficiency enhancement of hydrocarbon film removal in the afterglow zone at relatively low temperature (300-420 K) it was decided to introduce up to 15% N_2O in molecular hydrogen. This was dictated by a wish to increase the a-C:H film erosion rate due to atomic oxygen, especially in the remote parts from plasma, and simultaneously to prevent oxide film formation on divertor metallic units.

An H_2/N_2O mass-spectrum (without DCGD) consisted of lines: molecular hydrogen H_2 (2 amu), atomic nitrogen N (14 amu), molecular nitrogen N_2 (28 amu), nitric oxide NO (30 amu), and nitrous oxide N_2O (44 amu). When DCGD was switched on (current 30 mA, voltage 0.65 kV), the N_2O linear molecule decomposed into N_2, O, and NO. The N_2O line disappeared completely. In a carbon erosion product spectrum at sample location in the afterglow region there were H_2 (2 amu) line, H_2O (17 and 18 amu) lines, CH_4 (15 and 16 amu) lines, CO (28 amu) line coinciding with N_2 one, and CO_2 line coinciding with N_2O one. The CO_2 (44 amu) line was identified quite well because in the H_2/N_2O initial spectrum the N_2O line was absent after the discharge was switched on owing to complete N_2O decomposition at currents more than 20 mA. CO and CO_2 turned out to be the main erosion gaseous products.

The measurements have shown that in the afterglow region the a-C:H film erosion rate did not practically depend on the N_2O content in H_2 under N_2O partial pressure changing from 3 to 7 Pa and H_2 partial pressure of 40 Pa (650 K). The a-C:H film erosion rate increased noticeably (from 1.2 to 27 nm/min) with the temperature (Fig. 4). The most sharp erosion rate increase in the afterglow region was observed under temperature increasing from 420 to 500 K. In our opinion, it is a beneficial effect that allows controlling and regulating the hydrocarbon deposit removal rate by means of temperature increasing of separate tokamak units. In the afterglow zone the erosion rate reached the values (2-8 nm/min) acceptable for tokamak cleaning from redeposited a-C:H films at 400-500 K.

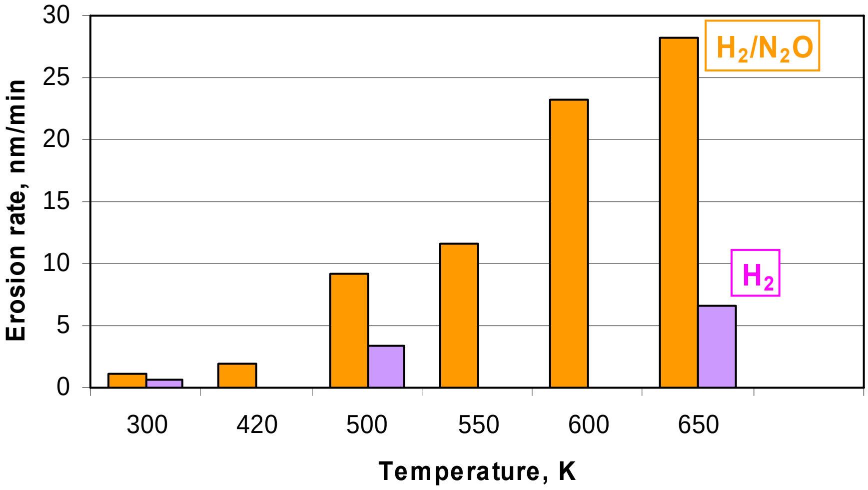


FIG. 4. Hard a-C:H film erosion rates in the H_2 and H_2/N_2O direct current glow discharges (23 mA, 0.6 kV) vs temperature at distance 11 cm from plasma boundary. H_2 and N_2O partial pressures are 40 and 7 Pa, respectively. Flow velocity is 1.2 m/s.

It should be noted that in the moving H_2/N_2O mixture the a-C:H film erosion occurred irregularly with formation of rounded inflations reminding of blisters. In inflation places the film peeled from the substrate. Hydrocarbon small particles were taken away by the gas flow and were a source of dust. After 40 min erosion in the afterglow zone (11 cm from plasma boundary) a 400 nm thick film was removed completely from Mo substrate (500 K). Carbon traces on the Mo substrate were not observed by EPMA. At the same time the Mo substrate was not oxidized in general. Oxygen traces on the smooth and free of defects surfaces were absent, but some parts of the surface, e. g., scratches formed at previous polishing, were covered with oxides. For removal of 1 μm thick hard a-C:H film located in the afterglow region, i.e., in the shadow of plasma, it needed ~8 h at 420 K and ~2 h at 500 K. At the same time on the cylindrical SS anode a yellow thin film appeared that consisted of Fe and Cr oxides. The problem of oxygen-containing plasma interaction with ITER metallic units required a special research.

In that way, DCGD in H_2(40 Pa)/ N_2O(3-7 Pa) mixtures is an effective method of hard a-C:H film erosion. The technique suggested is one of possible variants of an effective gas-discharge technology for hydrocarbon deposit removal from the remote parts of ITER divertor plasma.

3.3. Carbon deposition suppression in H_2/CH_4 DCGD at introducing of N_2O in mixture

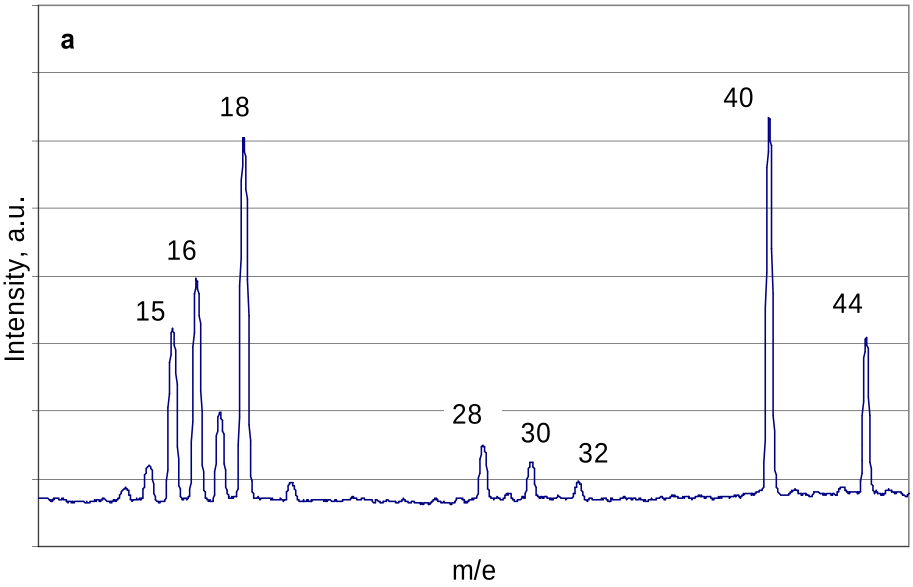
For studying of N_2O inhibitory properties regarding to a-C:H film deposition in DCGD (with the hollow anode) an N_2O admixture was introduced in H_2/CH_4 mixture. An $H_2/CH_4/N_2O$ mass-spectrum (without DCGD) is depicted in Fig. 5a. Previously from our mass-spectrometric measurements it has been established that in H_2 and CH_4 mixture entering a discharge (30 mA, 0.8 kV) with mass velocities of gases 7 and 0.6 sccm, respectively, about third of inlet methane flow (~0.17 sccm) converts into heavier hydrocarbons (mainly C_2H_y, where y = 2, 4, 6). Another third of the methane flow (~0.23 sccm) transforms in solid hydrocarbon deposits on the walls of the hollow cathode and the quartz tube bounding the discharge positive column (EPMA data). The last part of the primary methane flow (~0.2 sccm) leaving the discharge zone does not experience any transformations.

At introducing of a N_2O flow (~1 sccm) in the indicated mixture the methane flow leaving the discharge zone remained unchanged. At the same time the hydrocarbon film formation on the reactor wall was suppressed completely. In the hollow cathode and most part of positive column the carbon deposition was replaced by intensive film erosion. The C_2H_y flow decreased about two times.

In the discharge with the indicated parameters the primary N_2O (44 amu) molecules decomposed completely into N_2 (28 amu) and atomic oxygen. In the gas mixture leaving the discharge molecular oxygen (32 amu) (Fig. 5b) practically was absent. Most part of the atomic oxygen reacted with hydrogen and carbon forming H_2O (17 and 18 amu), CO (28 amu) and CO_2 (44 amu).

The mass-spectrum processing allowed also concluding that in the discharge zone nitrogen partly transformed into ammonia (NH_3, 16 and 17 amu) and cyanic acid (HCN, 27 amu). A cyanic acid yield constituted 10-15% of the primary methane flow.

Thus, it is shown that the addition of nitrous oxide in amounts slightly exceeded methane content to the H_2/CH_4 mixture practically completely suppressed the hydrocarbon deposition on the reactor wall. The methane flow leaving the discharge therewith remains unchanged (as in the case of the discharge in H_2/CH_4 mixture). The atomic oxygen enters in the reaction with “depositing” carbon giving CO and CO_2. At the same time molecular nitrogen transforms partly into ammonia and cyanic acid.



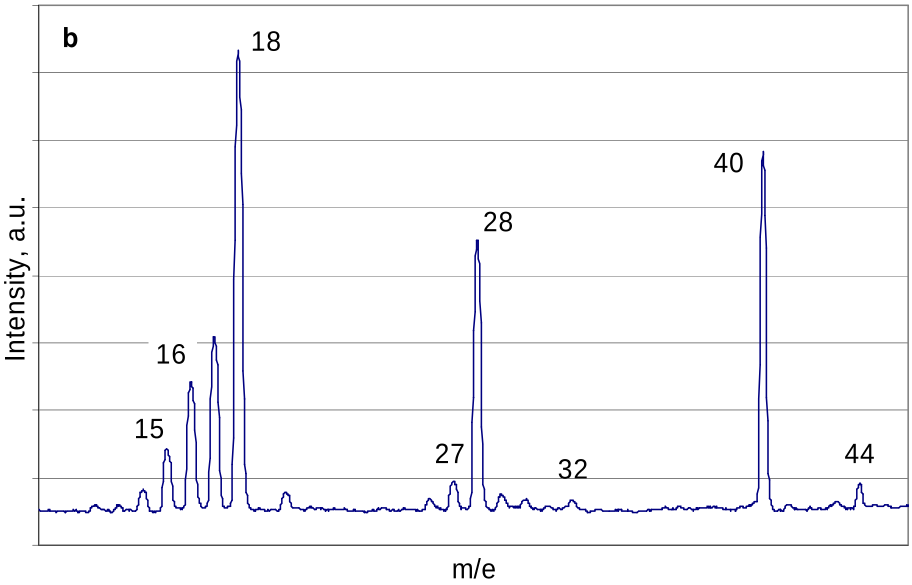


FIG. 5. a) $H_2/CH_4/N_2O$ mass-spectrum (without DCGD); b) plasmolysis products in $H_2/CH_4/N_2O$ discharge (30 mA, 0.8 kV). H_2,CH_4 and N_2O partial inlet pressures are 8, 1.5 and 2 Pa, respectively. Flow velocity is 4 m/s.

4. Conclusions

For studying of a-C:H film erosion in H_2 and H_2/N_2O mixture a stream technique was used.
In H_2 direct current glow discharge the C_2H_x and C_3H_x hydrocarbons appeared in the erosion products when a-C:H film interacted with plasma. The main a-C:H film gasification product is methane in the afterglow region. The hard a-C:H film erosion rate in the afterglow region decreased exponentially with distance from the atomic hydrogen source. The a-C:H film removal technique by H atoms permits to use deuterium and methane as an erosion product for tritium separation. The disadvantage of the hydrogen discharge is low erosion yields at 320-420 K (Y≈0.001 at.C/at.H) in the remote parts of ITER divertor plasma.
For efficiency enhancement of hard hydrocarbon film removal the H_2/N_2O gaseous mixture was proposed. In the afterglow zone the carbon gasification rate increased due to in parallel

proceeding reactions with formation of CH_4, CO, CO_2, and H_2O. For H_2/N_2O discharge the a-C:H film erosion rate in the afterglow zone (11 cm from plasma) was 4 times higher than for hydrogen discharge at 650 K.

After hydrocarbon film removal, island-like oxide films were formed on Mo substrate surface. An average oxide thickness decreased after improvement of surface treatment quality.

The addition of N_2O, which slightly exceeded methane content, in H_2/CH_4 direct current glow discharge suppressed completely a-C:H film deposition. The main plasmolysis products were CO, CO_2, and H_2O.

However, for using of plasma cleaning (on the base of H_2/N_2O mixture) of large machines from carbon films redeposited it is necessary to carry out a systematic investigation of possible effects connected with oxidizing and oxihydrogenating of divertor material surface layers (especially stainless steel and beryllium).

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[1] JANESCHITZ, G., et al., "Plasma-wall interaction issues in ITER", J. Nucl. Mater. **290-293** (2001) 1.

[2] ROTH, J., et al., "Flux dependence of carbon erosion and implication for ITER", J. Nucl. Mater. **337-339** (2005) 970.

[3] SHIMADA, M., et al., "Overview of goals and performance of ITER and strategy for plasma–wall interaction investigation", J. Nucl. Mater. **337-339** (2005) 808.

[4] FERREIRA, J.A., et al., "Alternative cleaning technique for the removal of carbon deposits", J. Nucl. Mater. **363-365** (2007) 888.

[5] VARSHAVSKAYA, I.G., et al., "Influence of 200 kHz electric discharge parameters on properties of diamond-like films deposited from methane", Materials Sciences Transactions **No 9** (2004) 19 (in Russian).

[6] MAYER, M., et al., "Carbon erosion and deposition on the ASDEX Upgrade divertor tiles", J. Nucl. Mater. **337-339** (2005) 119.

[7] VIETZKE, E., et al., "The reaction of atomic hydrogen with a-C:H and diamond films", Surf. Coat. Technol. **47** (1991) 156.

[8] WITTMANN, M., et al., "A model of hydrogen impact induced chemical erosion of carbon on elementary reaction steps ", J. Nucl. Mater. **227** (1996) 186.

[9] VIETZKE, E., et al., "Chemical erosion of amorphous hydrogenated carbon films by atomic and energetic hydrogen", J. Nucl. Mater. **145-147** (1987) 443.

[10] SCHWARZ-SELINGER T., et al., "Novel method for absolute quantification of the flux and angular distribution of a radical source for atomic hydrogen", J. Vac. Sci. Technol. **A18(3)** (2000) 995.