Removal of hydrogenated carbon deposits formed in fusion reactors with carbon walls by reactive oxygen particles

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Abstract. A method for removal of hydrogenated carbon deposits from the walls of fusion reactors with carbon divertors is presented. The method is based on interaction of neutral oxygen atoms with deposits at elevated temperatures typically found in such fusion reactors. The source of neutral oxygen atoms is oxygen plasma created with electrodeless high frequency discharges. The density of oxygen atoms in such plasma may approach 10^{22} m^{-3} making such discharges suitable for removal of deposits in huge systems like tokamaks.

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Introduction

Nuclear fusion is a promising source of energy for future generations. Although encouraging results have been obtained in past decades, there are technological problems that should be solved in the next future in order to allow for stable operation of future large fusion reactors. A yet unsolved problem arises from the fact that plasma facing components are subjected to extreme loads due to bombardment with energetic plasma particles. The problem is particularly severe in the divertor region of modern tokamaks. Currently, the divertors are often covered with tungsten or carbon tiles. Both materials have advantages and drawbacks. The major advantage of tungsten is its immunity to sputtering by light ions, and the major drawback comes from the simple fact that tungsten is a high Z material. Even minute quantities of tungsten in hot plasma cause important perturbations. Carbon, on the other hand, can be tolerated to much higher concentrations in hot plasma, but a major disadvantage preventing applications of this material is chemical sputtering [24]. Hydrogen ions as well as neutral atoms interact chemically with carbon coatings causing formation of CH_x radicals that tend to condensate in remote parts of fusion reactors causing formation of hydrogenated carbon films. This effect not only causes erosion at most exposed parts leading to modifications in geometry, but is extremely unwanted due to accumulation of radioactive tritium. Another disadvantage of carbon is its poor ability to recovering the original thermo-electrical properties disturbed by continuous irradiation with fast neutrons. In spite of these obvious

drawbacks carbon fibre composite remains the material of choice in the first stage of ITER operation. Obviously, the problem of removal of the deposits remains and should be solved in such a way that the quantity of deposits remains within tolerable limits. In other words, a method for suppression and/or removal of hydrogenated carbon deposits should be developed [7].

Among the proposed techniques for removal of hydrogenated carbon deposits, oxidation seems an especially attractive option [25]. It is well known that oxygen molecules interact with carbon containing materials at elevated temperatures. A problem arises from the fact that the temperature in ITER will be limited to 513 K [7], which is not enough for successful application of thermo-oxidative techniques. The potential barrier for chemical reaction between thermallized oxygen molecules at elevated temperatures is obviously too high.

An alternative to oxidation by oxygen molecules is application of oxygen atoms. The corresponding potential barrier for chemical interaction between neutral oxygen atoms and hydrogenated carbon is substantially lower so neutral atoms interact with such materials already at room temperature, and the interaction becomes reasonably intensive at elevated temperatures [18, 33]. Oxidation is therefore likely to appear. If the flux of oxygen atoms is large the surface will quickly saturate with oxygen functional groups [28, 33]. The next treatment effect is breaking of bonds between C atoms in hydrogenated carbon materials [20] and thus removal of hydrogenated carbon deposits. The reaction products (mainly carbon dioxide and water) desorb from surfaces and are pumped away from the system [16]. Treatment of deposits by neutral oxygen atoms therefore looks an attractive technology for application in fusion reactors with carbon walls.

Oxidation of hydrogenated carbon materials by neutral oxygen atoms has been used for decades in order to modify surface properties of organic materials [29, 30]. The technique has been applied successfully in different branches ranging from biomedicine [8, 6, 34] to nanoscience [11]. It has been also shown that the oxidation by neutral oxygen atoms is rather selective: not all hydrogenated carbon materials are etched at the same rate [9, 21]. Furthermore, experiments with composites based on polymer matrix showed that inorganic materials are unlikely to be affected by oxygen atoms providing the sample temperature is not too high [27]. Oxidation of hydrogenated carbon materials by neutral oxygen atoms is thus a promising technique for application in fusion reactors and extensive research is carried on within Euratom programme.

Experimental results

While a variety of sources of neutral oxygen atoms have been developed, low-pressure oxygen plasma seems to be superior in terms of reliability. Neutral oxygen atoms are created in oxygen plasma predominantly by dissociation of parent molecules at electron impact. Since oxygen molecules have two metastable states with excitation energy of about 1 and 2 eV, the threshold for dissociation is comfortably low. Oxygen atoms are thus produced in large quantities in plasma created by many
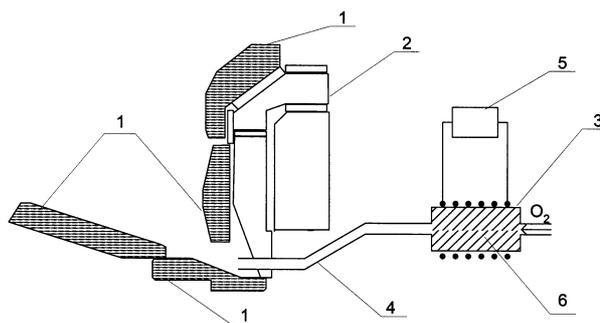

Fig. 1. Scheme of the proposed neutral oxygen atom delivery system for ITER: 1 – divertor tiles; 2 – reactor inner wall; 3 – discharge tube; 4 – connection tube; 5 – high frequency generator; 6 – plasma.

discharges. O atoms are perfectly stable in vacuum (recombination to molecules in the gas phase may occur only at elevated pressure since a three-body collision is required due to conservation of momentum and energy), they tend to recombine on the walls of discharge chamber. The probability for surface recombination depends enormously on the type and surface finish of the material facing plasma. The best material is probably glass since the recombination coefficient is rarely above 0.001 [12]. Other materials have different recombination coefficients and it is practically impossible to draw a general rule. Some metals including copper, nickel, iron and cobalt exhibit catalytic activity towards surface recombination of oxygen atoms. Those which tend to form stable oxides like aluminum and beryllium, on the other hand, have rather low recombination coefficients but it seems that the probability for surface recombination on well-oxidized aluminum depends on temperature. Furthermore, the morphology of such oxides usually also influence the probability, special in the case the oxides are porous. Such porosity is unlikely to occur when glass materials are used. An appropriate source of O atoms is therefore a discharge vessel made from glass. Any connection between the discharge tube and the reaction chamber with hydrogenated carbon deposits should be also made from a material with a low coefficient for heterogeneous recombination in order to minimize the loss by surface reactions. Figure 1 represents a schematic of a remote plasma reactor connected to the divertor region of ITER.

The requirement of having the discharge chamber made from glass dictates the choice of discharge for plasma ignition and sustentation. Since all metals exhibit relatively large probability for heterogeneous surface recombination, the discharge should be electrodeless. Apart from some technologically unsuitable discharges, two types of discharges are particularly worth mentioning: an inductively coupled radio frequency (RF) and a microwave discharge. Schematic of both discharges is presented in Fig. 2.

Both types of discharges are capable of sustaining oxygen plasma with an appreciably large concentration of neutral oxygen atoms. Microwave discharges in both cavity [4, 10, 26, 32] and surfatron [22] modes are capable of sustaining plasma with the dissociation fraction of well over 10%. The same applies for electrodeless radio frequency discharges [14, 15].
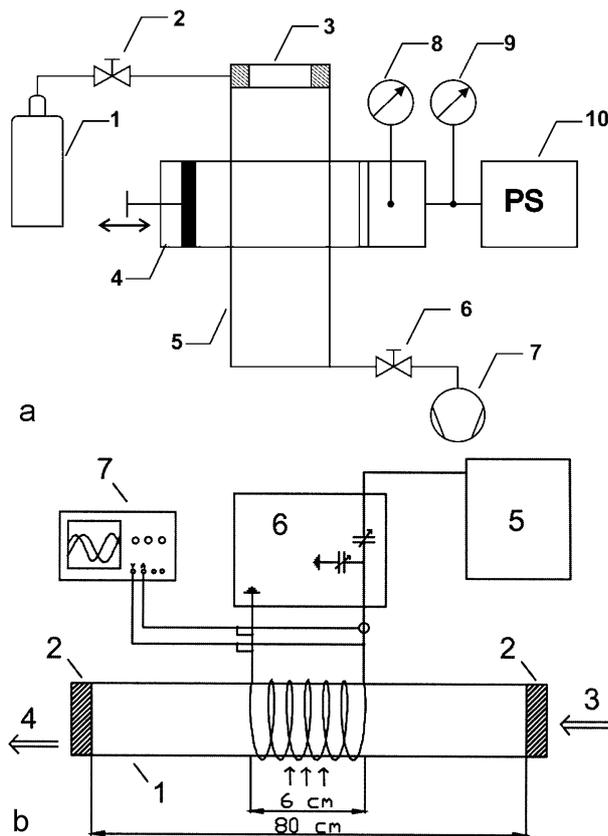
Fig. 2. Scheme of a microwave (a) and RF (b) plasma system. (a) 1 – oxygen flask; 2 – leak valve; 3 – CaF$_2$ window; 4 – MW resonator; 5 – discharge tube; 6 – valve; 7 – rotary pump; 8 – reflected power meter; 9 – nominal power meter; 10 – MW generator. (b) 1 – glass tube; 2 – kovar flange; 3 – gas inlet; 4 – pumping; 5 – RF generator; 6 – matching network; 7 – oscilloscope.

A variety of techniques for quantitative determination of the density of O atoms in plasma as well as in a flowing afterglow have been used. The techniques include chemical titration [23], actinometry [2, 3, 5], laser induced fluorescence [19], and catalytic probes [1, 13, 15, 31, 32]. The latter are particularly suitable for application in order to study local variations in a reactor loaded with samples of hydrogenated carbon deposits. Schematic of the catalytic probes is presented in Fig. 3. Basically, two types of catalytic probes are applicable: simple thermocouple probes and fiber-optics probes. The first type is suitable for determination of O atom density in a broad range, also at rather low dissociation fraction, but often fails in high-frequency discharges because of the electromagnetic interferences. The latter type is immune to such stray effects because the connection between the catalytic tip and the detection electronics is optical. Unfortunately, however, currently available optical fibers have rather poor transmission for infra-red radiation so the minimal temperature that could be detected is limited. Typically, fiber optics probes are capable of measuring temperatures above about 450 K so they fail in poorly dissociated oxygen – the signal is simply below the detection limit of the device.

The O atom density in the discharge chamber usually does not depend on the history of the plasma reactor as long as it is free from surface impurities. This is an important characteristic that does not hold for all gases.
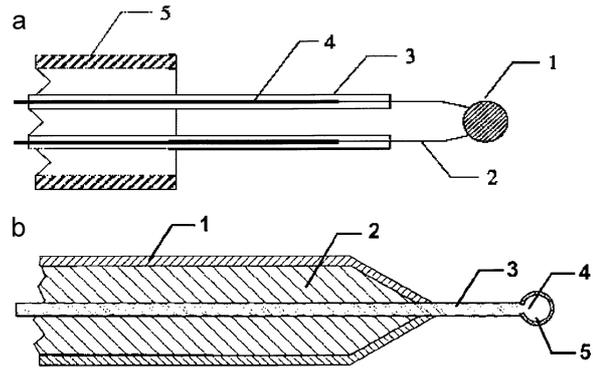

Fig. 3. Scheme of catalytic probes: a simple thermocouple probe (a) and a more sophisticated fiber-optics catalytic probe (b). (a): 1 – catalytic tip; 2 – thermocouple wire; 3 – kovar wire; 4 – thin glass tube; 5 – probe housing. (b): 1 – outer probe housing; 2 – inner probe housing; 3 – optic fiber; 4 – glass sphere; 5 – catalytic foil.

The effect is especially important when using hydrogen as the source gas [17]. In a side tube where plasma is absent, the O atom density decreases with increasing distance from the source (plasma). Figure 4 represents two examples on the behavior of O atoms in a side tube.
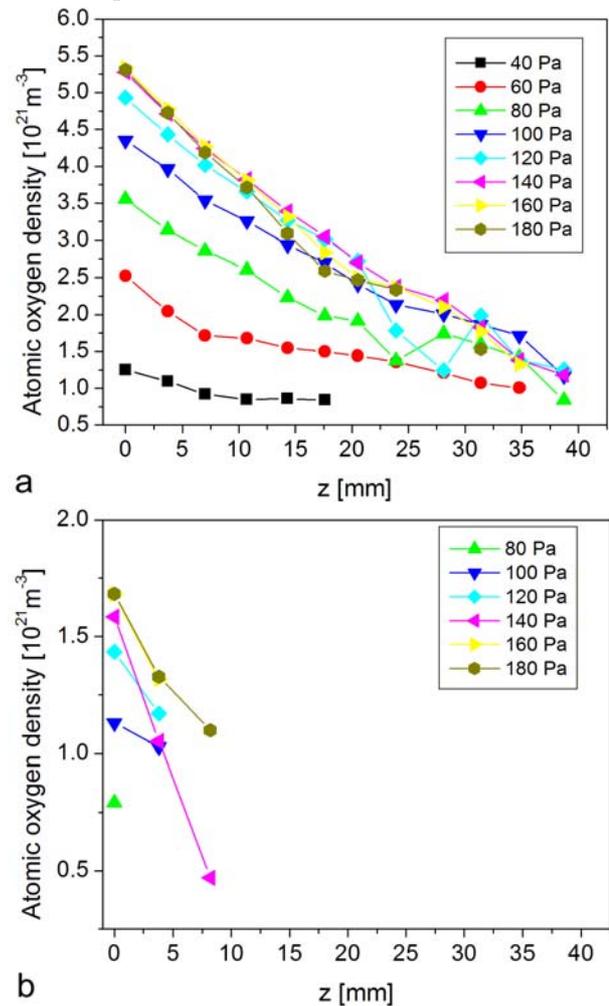

Fig. 4. Behavior of the O atom density in a glass tube open to the source of atoms on one side and terminating with two different materials on the other side. Closed with a teflon disc (a) and with a nickel disc (b). In the case of the nickel disc, the densities of O atoms drop very quickly below the level of detection due to the high recombination coefficient.
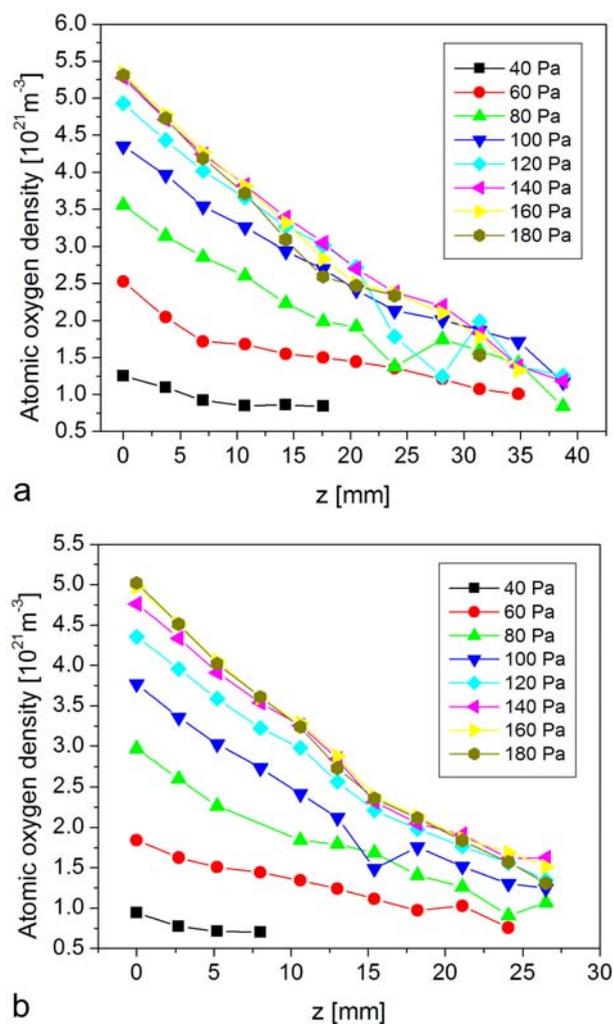
Fig. 5. Density of O atoms in a tube made from glass (a) and amorphous carbon (b).

In the first example, the O atom density was measured in a tube terminated with a material with a low recombination coefficient, while in the second case a material with a high recombination coefficient was placed at the closed end of the side tube. A huge difference is merely a consequence of extensive heterogeneous surface recombination of a nickel disc. As mentioned earlier, the probability for heterogeneous surface recombination of neutral oxygen atoms on oxidized nickel surface is large. In fact, nickel is a preferred material for manufacturing the catalytic tip of the probe.

The density of O atoms depends also on the recombination on the surfaces along the tube. Figure 5 illustrates this fact. The results represented in Figs. 4 and 5 are extremely important for removal of hydrogenated carbon films in gaps. It is well known that first wall materials in the ITER divertor will be castellated. Reasonably large removal rates will be obtained only by application of large quantities of O atoms at such structures. Otherwise, atoms would be just lost due to extensive surface recombination. Poor results presented in Fig. 4b are simply due to the fact that the probe sensitivity is too low to detect low density of O atoms. Nickel really represents a large sink for O atoms since the probe signal becomes immeasurably low already at the depth of few mm. Obviously, the detection limit

of the fiber optics catalytic probe in this particular configuration is at about 1×10^{21} m^{-3}. The detection limit depends on particular experimental conditions and is often governed by the thermal conductivity of the surrounding gas. The detection limit is improved at lower pressure, where the dissociation fraction of oxygen molecules increases linearly with decreasing pressure at a fixed density of neutral oxygen atoms.

Once the important issues about creation and loss of neutral oxygen atoms are understood and a technique for real time measurements of their density is elaborated the experiments on removal of hydrogenated carbon films are feasible. Figure 6 represents a typical result. The diagram in Fig. 6 represents the removal rate of the deposit vs. the sample temperature, while the photo in this figure confirms the ability of removal in a gap. Namely, the covered part of the sample presented in the photo is left practically intact while the bright central part of the sample is free from deposits due to extensive interaction with oxygen atoms. A radio frequency discharge was used as a source of O atoms and their density above the sample was determined by a fiber optic catalytic probe and was 2×10^{21} m^{-3}. The removal rate shown in the diagram in Fig. 6 indicates strong temperature dependence: at room temperature it is immeasurably low while at temperatures above 200°C it becomes suitably large and increases well with
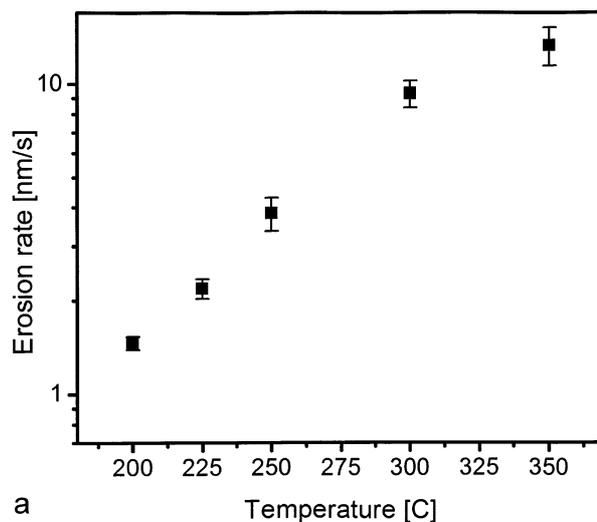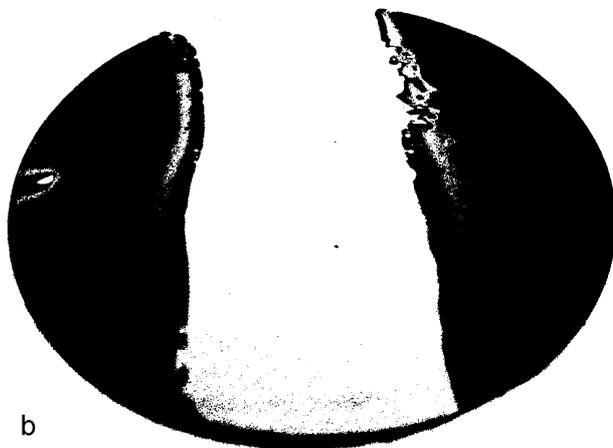
Fig. 6. The removal rate of hydrogenated deposits vs. sample temperature (a) and a photo of a sample placed into a gap after successful treatment (b).

increasing temperature. Since the ITER will operate at the temperature at the temperature of about 300°C the removal rate in the tokamak will be about 10 nm/s, making this technology suitable for practical application.

The removal rate for hydrogenated carbon deposits as presented in Fig. 6 is similar to values obtained for many polymers. The removal rate probably depends on the type of particular hydrogenated carbon deposits. The deposits reported in this paper were prepared by sputtering of a high-purity graphite target in reactive atmosphere of acetylene. The hydrogen content in the film was estimated to about 50 atomic percent. The removal rate probably depends on the hydrogen content, and also on the structure of the film deposited. In tokamaks with graphite walls a variety of deposits were reported. The range is really wide – from the so-called hard to soft deposits. The major difference is in hydrogen concentration. It is small in hard and large in soft deposits. In fact, the hard deposits are similar to films prepared by sputtering of graphite in the absence of reactive gas (sputtering by argon ions), while the soft deposits may have similar structure as some polymers. The difference in removal rates between these two extremes should be large. Obviously, soft deposits are etched at much higher rates than hard ones. Here, it is worth stressing a very high etching selectivity when neutral oxygen atoms are applied. Numerous authors have showed that different organic materials are etched at different rates. Even polymers with the same composition but different structure are etched at different rates. Recent results show an important role of the crystallinity degree as well as the surface morphology, density and possible porosity. The etching rate for different polymers may vary for orders of magnitude which is just another confirmation of an excellent etching selectivity obtained when using neutral oxygen atoms in the ground state as the etching medium.

Such extremely large etching selectivity represents an important advantage of oxygen atoms over other means of hydrogenated carbon removal. Namely, for practical application in fusion reactors the goal is effective removal of soft hydrogenated carbon deposits containing large quantities of fuel (hydrogen isotopes). The hard deposits can be tolerated in fusion reactors due to rather low concentration of hydrogen. Furthermore, etching selectivity is required because the carbon tiles should be preserved. In the ideal case, the original material from which the tiles facing plasma are made should be left intact. Application of neutral oxygen atoms in the ground state for removal of hydrogenated carbon deposits assures for fulfilling such requirements since the etching rate of carbon fiber composites is orders of magnitude lower than for most polymers. As mentioned above, the etching rate of many polymers is similar to the rate at which soft hydrogenated carbon films are etched.

Another advantages of application of neutral oxygen atoms for removal of hydrogenated carbon deposits is a simple fact that atoms diffuse anywhere in the vacuum vessel and can therefore be used right where they are needed – where hydrogenated carbon deposits accumulate. Of course, it is best to apply the oxygen atom jets at places where thick films are expected to be formed, but since the atoms are perfectly stable in vacuum or at low pressure they can diffuse also to remote parts of a tokamak chamber. Practically the only mechanism for neutral oxygen atom loss is heterogeneous surface recombination. As mentioned earlier, the probability of such recombination depends enormously on the type of material. Happily enough, the loss of atoms on the deposits themselves is not high. Recently published results estimate the loss by recombination to be less than an order of magnitude larger as compared to the loss by chemical reactions (oxidation of hydrogenated carbon to CO_2 and H_2O molecules). The recombination coefficient for stainless steel (a material that will be used for construction of the ITER tokamak) is an order of magnitude lower than for catalytic metals (Fig. 4b). Recombination on stainless steel is therefore considered the most important mechanism of neutral oxygen atom loss. In order to minimize this effect it is recommended to puff oxygen atoms close to the areas where the soft deposits are likely to occur. The recombination on other materials that are likely to be presented in ITER (beryllium, for instance) should be less important due to a low recombination coefficient for heterogeneous surface recombination.

Figure 5 represents interesting results on loss of O atoms along tubes made from two different materials: borosilicate glass and hydrogenated carbon. The results of systematic measurements of O atom density along these tubes by fiber optics catalytic probes are summarized in left and right diagram for glass and hydrogenated carbon, respectively. There is a definite difference in oxygen atoms density between the two examples (the x-axis values are only up to 27 mm along the tube covered with a hydrogenated carbon film), but the difference is not dramatic. Comparison of both diagrams allows for a qualitative conclusion that the O atoms diffuse deep into tubes made from both materials, and the difference in recombination coefficient for glass and hydrogenated carbon is not very big. In fact, the recombination coefficients are of the same order of magnitude – 10^{-3}.

It should be mentioned that surface recombination is not the only mechanism of O atoms loss on the tube covered with the hydrogenated carbon deposit. As shown in Fig. 6, the atoms are also lost by chemical reactions. Nevertheless, the loss by chemical reactions is less important than by heterogeneous surface recombination. All experiments with O atoms loss (Figs. 4 and 5) were performed at room temperature where the etching rate of hydrogenated carbon deposits is immeasurably low (Fig. 6).

Summary and conclusions

Removal of hydrogenated carbon deposits by neutral oxygen atoms is a suitable technique for conditioning ITER reactor as long as it operates with carbon divertors. Neutral oxygen atoms have an important advantage over charged oxygen particles: they can be produced in large quantities in a remote source and leaked into the main tokamak chamber without a substantial loss. They can also survive well in gaps and closed tubes as long as they are made of a material with

a low probability for heterogeneous surface recombination. Charged particles would not survive the transport from a remote source due to very high probability for surface neutralization. Also, ITER reactor will not allow for *in-situ* creating of a glow discharge (a common method for removal or organic impurities from surfaces of inorganic materials) due to the strong and permanent magnetic fields. Neutral O atoms are not sensitive to such magnetic fields so they can be delivered anywhere as long as the effective pumping speed is large enough and the connecting tube between the source (a high frequency discharge) and the tokamak chamber is made from a material with a low coefficient for heterogeneous surface recombination. The best materials are different types of glasses such as borosilicate glass and quartz glass. An alternative to glasses is application of ceramics such as alumina. The loss of O atoms by surface recombination for alumina is comfortably low at room temperature providing the material is highly polished. Very rough materials (such as those prepared by powder sintering) should be avoided as the recombination coefficient importantly depends on the surface morphology. Due to huge ITER dimensions large sources of O atoms will have to be developed. Such a development is currently conducting within EDFA activities.

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